

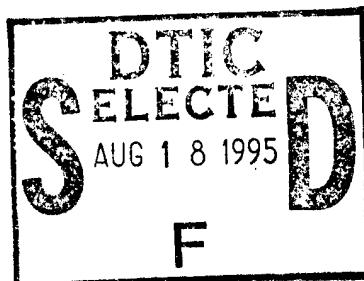
WL-TR-94-4126

REQUALIFICATION OF WHITE THERMAL
CONTROL COATINGS



YOSHIRO HARADA
MUKUND DESHPANDE

IIT RESEARCH INSTITUTE
10 WEST 35TH STREET
CHICAGO, IL 60616



OCTOBER 1994

FINAL REPORT FOR 11/15/91-10/15/94

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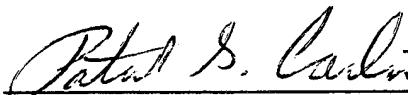
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Patrick S. Carlin
Project Engineer
Nonstructural Materials Branch



Kent J. Eisenbraut, Chief
Nonstructural Materials Branch



Charles E. Browning, Director
Nonmetallic Materials Division

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*Form Approved
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1. AGENCY USE ONLY (Leave blank)			2. REPORT DATE OCT 1994		3. REPORT TYPE AND DATES COVERED FINAL 11/15/91--10/15/94		
4. TITLE AND SUBTITLE REQUALIFICATION OF WHITE THERMAL CONTROL COATINGS			5. FUNDING NUMBERS C F33615-91-C-5554 PE 62102F PR 1501 TA 03 WU 04				
6. AUTHOR(S) YOSHIRO HARADA AND MUKUND DESHPANDE			8. PERFORMING ORGANIZATION REPORT NUMBER IITRI C06756-F				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) IIT RESEARCH INSTITUTE 10 WEST 35TH STREET CHICAGO IL 60616			10. SPONSORING / MONITORING AGENCY REPORT NUMBER WL-TR-94-4126				
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) MATERIALS DIRECTORATE WRIGHT LABORATORY AIR FORCE MATERIEL COMMAND WRIGHT PATTERSON AFB OH 45433-7734							
11. SUPPLEMENTARY NOTES							
12a. DISTRIBUTION / AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE: DISTRIBUTION IS UNLIMITED.			12b. DISTRIBUTION CODE				
13. ABSTRACT (Maximum 200 words) The IIT Research Institute (IITRI) supplies the aerospace community with three spacecraft thermal control coatings: S13G/LO-1, YB-71 (ZOT), and Z93, all of which incorporate inorganic potassium silicate as a component in their compositions. However, the particular potassium silicate being used, "PS7", is no longer manufactured. The objective of this requalification program was to develop coating formulations with a new silicate binder/encapsulant material. Encapsulation studies for S13G/LO-1 were conducted to obtain a stabilized ZnO pigment for this silicone binder formulation. With the inorganic Z93 and YB-71 formulations, the new silicate binder was to provide equal or improved optical and physical behavior for these compositions. Studies indicate that Kasil 2130 (PQ Corporation) is a satisfactory replacement in S13G/LO-1 and Z93. The development of formulation, processing and application techniques have yielded 2130-based S13GP/LO-1 and Z93P which show equivalent optical and physical behavior to their "PS7"-based predecessors. The suitability of Kasil 2130 as a binder in the zinc orthotitanate-pigmented YB-71 has not been clearly determined, and studies are being continued.							
14. SUBJECT TERMS Coatings, Space Environment, Satellite Thermal Control, Potassium Silicate, Radiation Effects					15. NUMBER OF PAGES 108		
					16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED		20. LIMITATION OF ABSTRACT UL	

TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES	iv
LIST OF TABLES	vii
FOREWORD	ix
ACKNOWLEDGEMENTS	x
EXECUTIVE SUMMARY	xi
1. INTRODUCTION	1
2. TECHNICAL BACKGROUND	
2.1 Pigment Screening	3
2.2 Binder Studies	5
2.3 Coatings Development	7
2.3.1 S13G	9
2.3.2 S13G/LO	11
2.3.3 S13G/LO-1	11
2.4 Space Environment Effects	11
3. RESULTS AND DISCUSSION	18
3.1 Materials Selection and Acquisition	18
3.1.1 Evaluation of Potassium Silicate Binders	18
3.2 Reformulation Studies	34
3.2.1 Z93	34
3.2.2 YB-71	37
3.2.3 S13G/LO-1	37
3.3 Coating Properties	44
3.3.1 Optical Properties	45
3.3.2 Torsion Resistance	59
3.3.3 Thermal-Vacuum Testing - Humidity Resistance	66
3.3.4 Outgassing Properties	73
3.4 Environmental Testing	73
3.4.1 Marshall Space Flight Center (Jason Vaughn, EH11)	81
3.4.2 Wright Laboratory (Pat Carlin)	87
3.4.3 Aerospace Corporation (Mike Meshishnek)	87
3.4.4 Loral Vought Systems (Joe Stoyack)	89
3.5 Space-Flight Testing	89
4. SUMMARY AND CONCLUSIONS	91
5. RECOMMENDATIONS FOR FUTURE WORK	92
6. REFERENCES	94

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	UV Degradation of S13	8
2	UV Degradation of ZnO	8
3	UV Degradation of Z93	10
4	UV Degradation of Silicate-treated ZnO	10
5	Solar Absorptance vs. Equivalent Sun Hours for Different Resin Systems	12
6	Long Duration Exposure Facility Thermal Control Surface Experiment	17
7	Reflectance of Sample 7: Z-93/PS-7 Original Formulation	46
8	Reflectance of Sample 8: Z-93/PS-7 Original Formulation	46
9	Reflectance of Sample 9: Z-93/PS-7 Original Formulation	47
10	Reflectance of Sample 19: Z-93/2130	47
11	Reflectance of Sample 20: Z-93/2130	48
12	Reflectance of Sample 21: Z-93/2130	48
13	Reflectance Data of Sample MM51: Z-93/Kasil-1	49
14	Reflectance Data of Sample MM52: Z-93/Kasil-1	49
15	Reflectance of Samples 13, 14, 18: YB-71/PS-7 Original Formulation	50
16	Reflectance of Sample 34: YB-71/2130	50
17	Reflectance of Sample 47: YB-71/2130	51
18	Reflectance of Sample 48: YB-71/2130	51
19	Reflectance Data: Sample MM61 (YB-71/Kasil-1)	52
20	Reflectance Date: Sample MM62 (YB-71/Kasil-1)	52

LIST OF FIGURES - CONTINUED

<u>Figure</u>		<u>Page</u>
21	Diffuse Reflectance Data. Comparison of New and Old YB-71	57
22	Diffuse Reflectance Data. Comparison of New and Old S13G/LO-1	57
23	Reflectance Data of Sample MM94 (S13G/LO-1, Kasil 2130, Batch R-055) . . .	58
24	Reflectance Data of Sample MM95 (S13G/LO-1, Kasil 2130, Batch R-055) . . .	58
25	Solar Absorptance versus Thickness of Z-93P	60
26	Total Emittance versus Thickness for Z-93P	61
27	Solar Absorptance versus Thickness for S13GP/LO-1	62
28	Total Emittance versus Thickness for S13GP/LO-1	63
29	Torsion Test Apparatus	64
30	Schematic of Torsional Failure	65
31	Photograph of Sample IITRI-8 (Z93) After 13,733 Cycles of +65° to -95°C .	71
32	Photograph of Sample IITRI-10 (YB-71P) After 13,733 Cycles of +65° to -95°C	71
33	Photograph of Sample IITRI-5 (S13GP/LO-1) After 13,733 Cycles of +65° to -95°C	72
34	Photograph of Sample IITRI-1 (Z93P) After 13,733 Cycles of +65° to -95°C .	72
35	Diffuse Reflectance Data. S13G/LO-1 After PPPL Exposure	83
36	Diffuse Reflectance Data. S13G/LO-1 After AODTS Exposure	83
37	Diffuse Reflectance Data. S13GP/LO-1 After PPPL Exposure	84
38	Diffuse Reflectance Data. S13GP/LO-1 After AODTS Exposure	84
39	Diffuse Reflectance Data. YB-71 After PPPL Exposure	85

LIST OF FIGURES - CONTINUED

<u>Figure</u>		<u>Page</u>
40	Diffuse Reflectance Data. YB-71 After AODTS Exposure	85
41	Diffuse Reflectance Data. YB-71P After PPPL Exposure	86
42	Diffuse Reflectance Data. YB-71P After AODTS Exposure	86

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Effect of UV Irradiation in Vacuum on Optical Properties of Miscellaneous Inorganic Pigments	4
2 Effect of UV Irradiation in Vacuum on Optical Properties of Several Organic Coatings Pigmented with SP 500 ZnO	6
3 Solar Reflectors: Physical Properties	9
4 Solar Reflectors: Thermo-optical Properties	13
5 Changes in Solar Absorptance and Emittance After 5000 ESH Exposure	14
6 Specifications and Typical Properties Zaclon Potassium Silicates, Technical	19
7 Typical Composition and Properties of Liquid Kasil® Potassium Silicates	20
8 Product Specification - Kasil® 2130	21
9 PQ Corporation Certification	22
10 Product Specification - Kasil® 1	23
11 Certificate of Analysis	24
12 Solids Content of Candidate PQ Potassium Silicates and PS7	25
13 Quantitative Analysis of Potassium Silicates	27
14 Results of Titration Analyses for PS7 and Kasil 2130	28
15 pH of Potassium Silicate Solutions	29
16 NJZ Technical Information	30
17 Mixed Oxalate (MOX) Process for Synthesis of Zinc Orthotitanate	31
18 Semiquantitative Analysis of Zinc Orthotitanate Powders	32
19 Summary of Z93 Reformulation Experiments (R-003 to R-005)	35
20 Summary of Reformulation Efforts (R-016 to R-018)	36

LIST OF TABLES - CONTINUED

<u>Table</u>		<u>Page</u>
21	YB-71 Reformulation with Kasil 2130	38
22	Chemical Composition of Retain Samples Taken During Reactive Encapsulation of Zno (SP-500)	40
23	Chemical Composition of Reactively Encapsulated ZnO (SP-500), S13G, S13GP, S13GK	43
24	Optical Properties of Z-93 Formulations	53
25	Optical Properties of YB-71 Formulations	54
26	YB-71 Sample Pre-exposure Solar Absorptance	55
27	Optical Property Data for IITRI Coatings	56
28	Results of Torsion Test for Z-93	67
29	Results of Torsion Test for YB-71 and Clone Formulations for YB-71-P and YB-71-K	68
30	Coating Samples for Thermal Vacuum Testing	69
31	Test Report for Mass Loss and Collected Volatile Condensable Materials	74
32	Results of AO-VUV Exposure of Thermal Control Coatings	82
33	Results of Vacuum-UV, Electron Irradiation of Thermal Control Coatings	88

FOREWORD

This Final Report No. IITRI-C06756-F, "Requalification of White Thermal Control Coatings," summarizes work performed under U. S. Air Force Contract No. F33615-91-C-5554, "Hardened Materials Validation/Spacecraft Coatings," over the period 1 November 1991 to 31 October 1994. The results of studies which were conducted to requalify solar reflector thermal control coatings for spacecraft are presented. The coatings include two inorganic materials, Z93 and YB-71, and an organic formulation, S13G/LO-1.

The Project Engineer on this program was Patrick S. Carlin, WL/MLBT, Wright Patterson AFB, OH.

Respectfully submitted,

IIT RESEARCH INSTITUTE



Yoshiro Harada
Sr. Materials Scientist
Advanced Materials & Coatings

Approved:



G. C. Sresty
Manager
Energy & Environmental Sciences



Mukund Deshpande
Research Engineer
Advanced Materials & Coatings

ACKNOWLEDGEMENTS

IIT Research Institute (IITRI) personnel who have contributed to this program include Tom Curtis, Alvin Ray, Jim Ross and Bill Sabato. Guggilam Sresty acted as Manager for this program. The valuable advice and guidance of Patrick S. Carlin, Project Engineer, WL/MLBT, are gratefully acknowledged. Thanks are due to the following organizations and personnel for their valuable contributions: NASA/Marshall Space Flight Center - Jim Zwiener, Jason Vaughn, Miria Finkenor, and Dave Edwards; NASA-Lewis Research Center - Joyce Dever; NASA-Goddard Space Flight Center - Lonnie Kauder; Swales & Associates - Patsy Dickens and Wanda Peters; Loral Vought Systems - Joe Stoyack; McDonnell Douglas Aerospace - Steve Daneman, Mark Hasegawa, and Hank Babel; AZ Technology - Donald Wilkes and Richard Mell; and University of Dayton Research Institute - Cliff Cerbus.

The support of the U.S. Air Force with Chief Engineer, Col. Juri Randmaa of SMC/SD and Col. Warren Riles, SMC/SDE, is gratefully noted. Other SMC/SDE personnel who have provided input to this program are Lt. Col. Kurt Johnson, Capt. Scott Simcox, and Lt. Quang Bui.

Special appreciation is extended to Jerry Bauer and Mike Meshishnek of the Aerospace Corporation. Mr. Bauer of the Vehicle Design and Manufacturing Department has lent strong support in funding resources and program guidance. Dr. Meshishnek of the Materials Evaluation and Survivability Department has provided valuable overall technical input to the program including space simulation testing and analyses of materials behavior.

EXECUTIVE SUMMARY

Background:

The optical characteristics of spacecraft surfaces are fundamental parameters in controlling its temperature. Passive thermal control coatings with designed solar absorptance and infrared emittance properties have been developed for various space conditions and environments. In this total environment, the coatings must be stable and maintain their desired optical and mechanical properties for the course of a particular mission ranging up to a design lifetime of thirty years.

The IIT Research Institute (IITRI) supplies the aerospace community with three coatings: S13G/LO-1, YB-71 (ZOT), and Z93, all of which incorporate inorganic potassium silicate as a major and a vital component in their compositions. In the case of the silicone-based S13G/LO-1, the silicate is used to reactively encapsulate the ZnO pigment particles, forming a barrier to photodesorption reactions on the surface of ZnO. In the case of the inorganic Z93 and YB-71, the silicate constitutes the binder component in the coatings. However, the particular potassium silicate that has been used, "PS7", is no longer manufactured by Sylvania.

Objective:

The objective of this program was to develop a silicate binder/encapsulant material which would be an appropriate replacement for PS7. The work encompassed evaluation of commercially available alkali silicates to determine their applicability for use in our standard coatings. Encapsulation studies for S13G/LO-1 were conducted with a view toward upgrading this chemical process to obtain the pigment product with greater efficiency and economy. The achievement of greater stability for the S13G/LO-1 formulation was also a goal of this study. With the inorganic Z93 and YB-71 formulations, the new silicate binder was to provide equal or improved optical and physical behavior for these compositions.

Summary:

Our studies to reformulate IITRI's solar reflectors—Z93, S13G/LO-1 and YB-71—have resulted in the following developments:

1. The substitution of PQ Corporation's Kasil 2130 for Sylvania's PS7 in the Z93 formulation produces coatings (Z93P) which are equivalent or superior to the original Z93 in physical, mechanical, and optical properties, and in stability to a simulated space environment.
2. The substitution of Kasil 2130 for PS7 in the encapsulation process for coating zinc oxide pigment particles, yields a S13GP/LO-1 composition which is equivalent in processing behavior and in properties to the original S13G/LO-1. In addition, a superior stability to the space environment is indicated for the reformulated silicone composition as compared to the older S13G/LO.
3. The use of Kasil 2130 as a binder replacement for PS7 in the YB-71 composition results in coatings (YB-71P) which exhibit processing behavior, physical, mechanical and optical properties similar to those for YB-71. However, YB-71P exhibits decreased resistance to optical degradation in a simulated space environment, particularly under electron irradiation.
4. The reformulated Z93P and S13GP/LO-1 incorporating Kasil 2130 appear to be satisfactory replacements for Z93 and S13G/LO-1 which utilized PS7. Additional studies are required to develop a YB-71P composition which will be as stable to the space environment as YB-71.

1. INTRODUCTION

The optical characteristics of spacecraft surfaces are fundamental parameters in controlling the spacecraft temperature. Passive thermal control coatings with designed solar absorptance and infrared emittance properties have been developed for various space conditions and environments. In a particular total environment, the coatings must be stable and maintain their desired optical and mechanical properties for the course of a particular mission ranging up to a design lifetime of 30 years.

Currently, IIT Research Institute (IITRI) supplies the aerospace community with three white coatings: S13G/LO-1, YB-71 (ZOT), and Z93, all of which incorporate inorganic potassium silicate as a major and a vital component in their compositions. In the case of the silicone-based S13G/LO-1, the silicate is used to reactively encapsulate the ZnO pigment particles, forming a barrier to photodesorption reactions on the surface of ZnO. In the case of the inorganic Z93 and YB-71, the silicate constitutes the binder component in the coatings. However, the particular potassium silicate being used, "PS7," is no longer manufactured by Sylvania.

The objective of this program was to develop a silicate binder/encapsulant material which would be an appropriate replacement for PS7. The work encompassed evaluation of commercially available alkali silicates to determine their applicability for use in our standard coatings. Encapsulation studies for S13G/LO-1 were conducted with a view toward upgrading this chemical process to obtain the pigment product with greater efficiency and economy. The achievement of greater stability for the S13G/LO-1 formulation was also a goal of this study. With the inorganic Z93 and YB-71 formulations, the new silicate binder was to provide equal or improved optical and physical behavior for these compositions.

Studies conducted on this program indicate that Kasil 2130 (PQ Corporation) is a satisfactory replacement for S13G/LO-1 and Z93. The development of formulation, processing and application techniques have yielded 2130-based S13GP/LO-1 and Z93P which show nearly equivalent optical and physical behavior to their "PS7"-based predecessors. The suitability of Kasil 2130 as a binder in the zinc orthotitanate-pigmented YB-71 has not been clearly determined.

2. TECHNICAL BACKGROUND

The temperature regulation of satellites and space vehicles is one of the most challenging technical problems confronting spacecraft designers and engineers. The ultimate objective of thermal design is to ensure that the spacecraft operates within the prescribed temperature range defined by the temperature limitations of the vehicle materials and components. The use of selectively-reflecting surface coatings as an integral part of passive thermal design has received the most attention of the techniques available. Overall thermal control is achieved by regulation of absorbed solar energy, solar absorptance, (α_s), and the ability to emit heat, thermal emittance, (ϵ). The ratio of these optical properties, α_s/ϵ , is the primary materials factor in spacecraft temperature control, and the goal is to achieve a stability in the solar absorptance, i.e., resistance to change in a space environment.

In the early days of spacecraft materials development, ultraviolet (UV) irradiation in vacuum testing was the principal means for evaluating optical stability. Additionally, the contributions of high energy electron and proton radiation, micrometeoroids and space debris, system-generated contamination and atomic oxygen (AO), were also recognized and addressed. The particularly degrading effects of AO have been observed from experiments on the Space Shuttle¹ and most recently from the Long Duration Exposure Facility (LDEF).

Our studies to develop spacecraft thermal control coatings for different missions have been directed primarily toward optical stability in this severe environment. In addition, our focus has been on coating systems which can be applied on relatively large surfaces under ambient conditions and also cured at room temperature. Maintaining the simplicity of the processing procedure was considered an important factor in obtaining desired materials reproducibility in optical and mechanical properties. Solar reflectors which have been developed at IITRI and have been used on space hardware are:

- (1) Z93:ZnO - potassium silicate
- (2) S13G/LO-1:silicate encapsulated ZnO - methyl silicone
- (3) YB-71:Zn₂TiO₄ - potassium silicate

A historical perspective of studies leading to these systems is provided in the following review.

2.1 PIGMENT SCREENING

The early studies consisted of ultraviolet-vacuum screening tests for a large number of white powders as potential solar reflector pigments.² These tests were performed so that the less stable materials could be eliminated rapidly from any extended study. Although much of this early work was performed prior to in situ reflectance measurements, the work is germane to the extent that (1) pigments and materials shown to degrade by post-exposure measurements performed in air have been shown to never have degraded less when the measurements were subsequently performed in situ in vacuum; and (2) generally only the semiconductor pigments have been found to be very sensitive to oxygen bleaching, and the data on the many dielectric pigments examined were largely useful, though generally disappointing.

The results of vacuum-UV tests for selected pigments presented in Table 1 show that considerable coloration occurred in most of the pigments. Representative reflectance values are given for two wavelengths in the visible spectrum, 440 and 600 m μ . For most of the early screening work, reflectance curves in the visible spectrum were sufficient to suggest or preclude additional study.

In general, natural, mined minerals were less affected by UV irradiation in vacuum than synthetic laboratory chemicals. Exceptions were zinc compounds and tin oxide. For example, natural wollastonite was superior to synthetic calcium silicate. A marked difference in stability was apparent among different crystal forms of the same material. Metastable gamma alumina and cubic (unstabilized) zirconia degraded much more severely than their stable counterparts, alpha alumina and monoclinic zirconia. Purity in itself was not correlatable with stability. It was shown for Al₂O₃ and ZrO₂ that a 99% purity powder could be more stable than 99.9% material. Stability to a UV-vacuum environment is the result of a number of different factors in addition to purity (particle size and shape, surface chemistry, ionic activity, thermal history).

TABLE 1. EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF MISCELLANEOUS INORGANIC PIGMENTS

Material	Manufacturer's Designation	Exposure ESH*	Reflectance, % 440 μm	Reflectance, % 600 μm
Al_2O_3	Alucer MC (alpha)	0 180	100.0 74.0	100.0 91.5
Al_2O_3	Alucer MA (gamma)	0 75	93.5 49.5	90.0 82.5
Sb_2O_3	--	0 75	92.5 36.5	96.5 50.0
BaCO_3	Reagent grade	0 200	98.5 71.0	99.0 93.5
BN	HC 0021	0 75	88.5 65.0	92.5 84.0
CaF_2	Reagent grade	0 200	94.5 61.0	97.0 87.5
CaSiO_3	Synthetic	0 75	86.0 58.0	90.0 81.0
CaSiO_3	Wollastonite C-1	0 75	92.5 81.0	94.5 91.5
MgAl_2O_4	Spinel	0 75	97.5 70.0	97.0 92.5
MgO	Reagent-grade powder	0 75	98.5 71.0	98.5 92.5
SiO_2	Diatomaceous earth, Dicalite WB-5	0 180	92.0 87.5	93.5 93.0
SiO_2	No. 7900 Vycor	0 200	94.0 43.0	95.0 44.5
SnO_2	CP	0 300	88.0 78.5	90.0 88.0
ZrO_2	CP (Monoclinic)	0 75	96.0 75.5	97.5 92.5
ZrO_2	Cubic	0 180	88.0 33.0	95.5 73.5
ZrSiO_4	Superpax	0 180	86.5 65.0	92.5 84.5
ZnS	Reagent grade	0 75	91.0 89.0	94.5 94.0
ZnO	SP 500	0 75	95.0 95.0	99.0 99.0

* ESH - Equivalent Sun Hours

The early studies showed zinc oxide to be the most stable pigment; subsequent work revealed the stability of the mixed oxide, Zn_2TiO_4 , to be similar to that of ZnO .^{3,4} A high purity zinc oxide trademarked as SP500 (New Jersey Zinc, now known as Zinc Corporation of America) was the material designated for Z93 and S13.

2.2 BINDER STUDIES

Early inorganic binder candidates were monoaluminum dihydrogen phosphate, colloidal silica and various alkali silicates.¹ In UV-vacuum tests of formulations involving zirconia as the pigment, the silicate systems exhibited the smallest change in solar absorptance after 200 ESH:

	$\Delta\alpha_s$
Sodium silicate	0.04
Potassium silicate	0.06
Colloidal silica	0.14
AlH_2 phosphate	0.11

The superior physical properties of silicate coatings compared to the soft silica formulations, along with room temperature curability compared to the 450°F needed for phosphates, made silicate binders the choice for extended studies. The choice of Sylvania's PS7 was based on the fact that it was the highest purity potassium silicate available commercially.

Screening of organic coating binders involved commercially available silicones, fluorine-containing aliphatic resins, and modified silicone-epoxy compositions. Table 2 shows the effect of UV irradiation in vacuum of several organic coatings. The superior resistance of methyl silicone resins was observed in these studies, and the study of experimental methyl silicone resins comprised a major portion of early investigations. The commercial silicone resin of choice was RTV602, a room temperature curing elastomer produced by General Electric.

TABLE 2. EFFECT OF UV IRRADIATION IN VACUUM ON OPTICAL PROPERTIES OF SEVERAL ORGANIC COATINGS PIGMENTED WITH SP 500 ZnO

Resin Binder	Exposure ESH	Reflectance, %	
		440 μm	600 μm
Teflon FEP 120/COP* of tetrafluoroethylene and hexafluoropropylene	0	84.2	77.3
	314	52.4	67.5
Viton A/COP of vinylidene fluoride and hexafluoropropylene	0	88.0	94.0
	108	68.0	87.5
Kel-F 800/COP of vinylidene fluoride and trifluorochloroethylene	0	84.0	77.5
	108	64.5	72.5
Kynar L-18/polyvinylidene fluoride	0	84.0	90.0
	108	64.0	81.0
Exon 461/COP of vinyl chloride and trifluorochloroethylene	0	85.0	80.5
	108	10.0	31.5
Leonite 201-S/silicone-epoxy modified acrylic	0	86.0	85.0
	108	71.0	83.0
806A/methyl phenyl silicone	0	89.0	87.5
	108	56.0	83.5
RTV-11/methyl silicone	0	91.0	92.0
	500	88.0	91.5
RTV-602/methyl silicone	0	91.0	93.5
	500	90.0	93.5

*Co-polymer

2.3 COATINGS DEVELOPMENT

All coating formulations contain three ingredients: pigment, binder, and enough diluent to achieve a sprayable consistency. The pigment-to-binder ratio (PBR) is maximized to achieve the highest reflectance attainable and to maximize UV-vacuum stability. The binder component is responsible for lower reflectance in the infrared, and may also be more susceptible to optical damage. The maximum pigment loading is governed by desired physical properties, i.e., if a harder inorganic surface is required, higher binder concentration is used. With silicone coatings, composition is dictated by the desired degree of elastomeric behavior and specularity.

Coatings which have been developed at IITRI are shown in Table 3, along with some of their properties. All of the coatings are applied by spray techniques and cured at room temperature. In general, excellent adhesion is achieved on metal surfaces such as aluminum or magnesium when appropriate substrate preparation is taken. Substrate preparation can be accomplished by mechanical abrasion to obtain higher surface area for improved bonding, or when such surface treatment cannot be tolerated, appropriate primers or coupling agents are used. Cleanliness is an extremely important consideration in the processing of coatings, both from the standpoint of good initial physical properties and of good optical stability in a space environment.

The S13G/LO-1 is a fourth generation material,⁵ reflecting evolutionary changes in testing, material requirements, and material availability. The original S13 consisted of a ZnO pigment (SP500/New Jersey Zinc) in a polydimethylsiloxane (RTV 602/GE). Evaluation of S13 using in situ measurements reveals a reflectance decrease of about 35% at 2000 nm (2 μ) after approximately 800 equivalent sun hours (ESH) of UV irradiation in vacuum (Figure 1). However, an essentially instantaneous increase in infrared reflectance occurs when either air or oxygen is admitted to the irradiated specimen; the recovery is very nearly total after only 2 minutes of exposure to air (Figure 1).

The effect of 1000 ESH of UV radiation on a pigment specimen of SP500 ZnO is shown in Figure 2. These data show that the bulk of the solar absorptance increase exhibited by ZnO as a powder, and as a paint in the S13 coating, is due to the oxygen-bleachable damage sustained in the infrared.

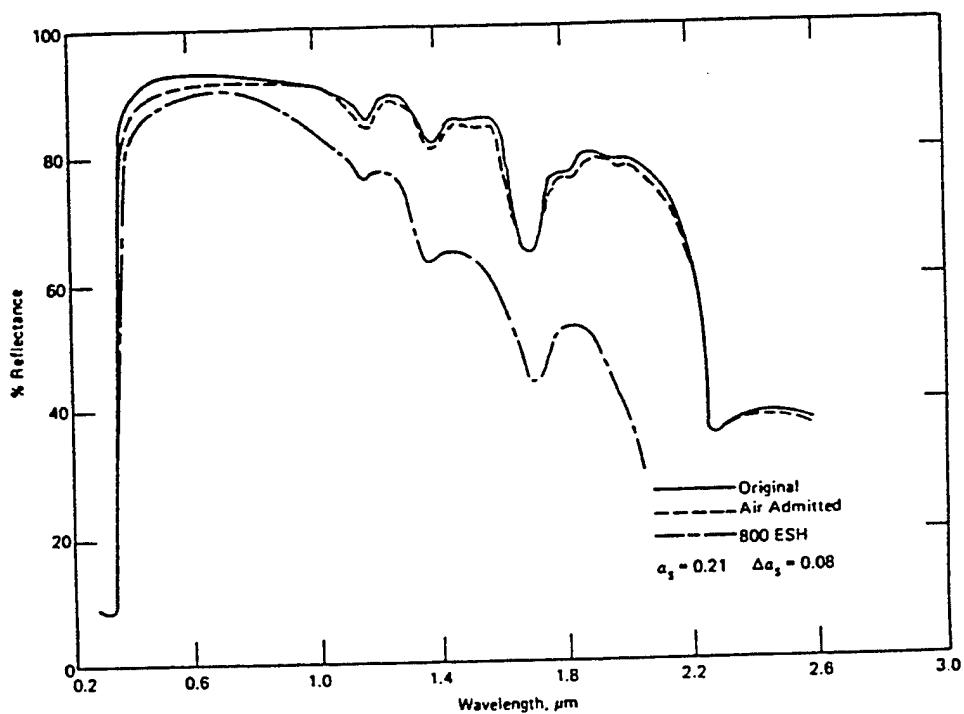


Figure 1. UV Degradation of S-13.

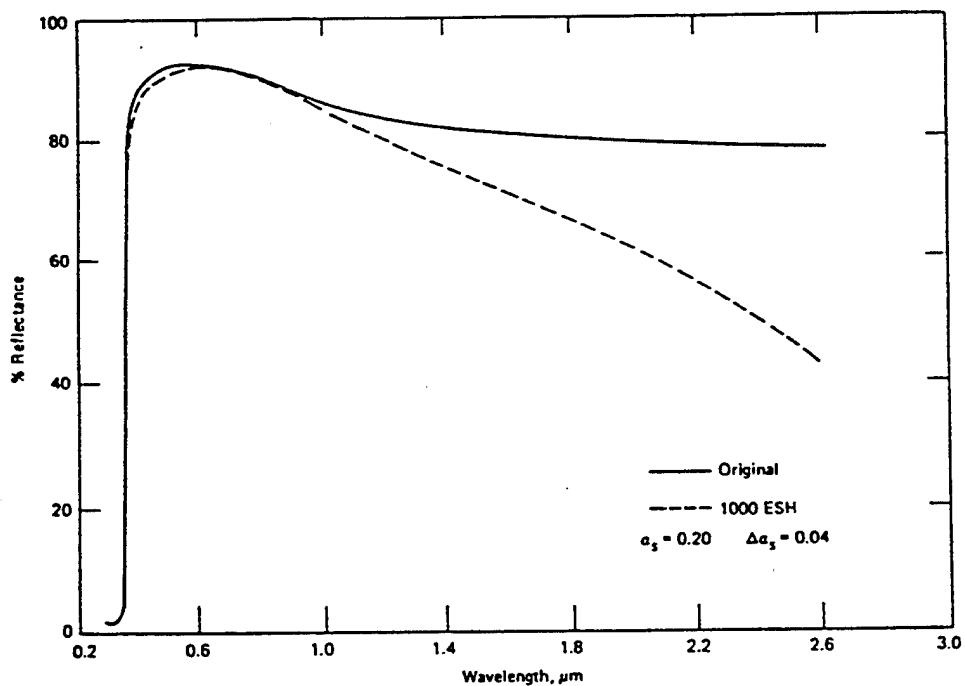


Figure 2. UV Degradation of ZnO.

TABLE 3. SOLAR REFLECTORS: PHYSICAL PROPERTIES

	Z93	S13G/LO-1	YB-71 (ZOT)
Composition	ZnO-potassium silicate	ZnO (encapsulated) - methyl silicone	Zn ₂ TiO ₄ -potassium silicate
Pigment-Binder Ratio	4.3:1	2.0:1	7.1:1
Application	Spray/RT	Spray/RT	Spray/RT
Handling	24 hours	4 hours	24 hours
Cure	7 days	7 days	14 days
Physical Behavior	Slightly flexible, hard surface	Very flexible, soft surface	Slightly flexible, very hard surface
Cleanability	Poor, protection required	Yes	Poor, protection required

The rapidity with which the UV-induced infrared absorption band develops in ZnO and the abruptness with which oxygen annihilates the absorption strongly indicates that the infrared phenomenon is not related to bulk diffusion phenomena but is associated with the photodesorption of absorbed oxygen. IITRI's Z93 thermal control coating, an SP500 ZnO-pigmented potassium silicate paint, did not undergo the bleachable infrared damage exhibited by S13 and pure ZnO. Figure 3 is a typical spectra of irradiated and unirradiated Z93, which is seen to be quite stable to UV radiation in vacuum.

2.3.1 S13G

The absence of damage to ZnO-pigmented alkali silicate coatings suggested that the reaction of ZnO with the potassium silicate may have precluded the bleachable infrared degradation exhibited by ZnO powder and ZnO-pigmented silicone paints. The polydimethylsiloxanes do not "wet" the pigment particles and consequently it was conjectured that they do not offer an effective barrier to photodesorption reactions on the surface of ZnO. A series of experiments were performed in which ZnO was first treated with potassium silicate

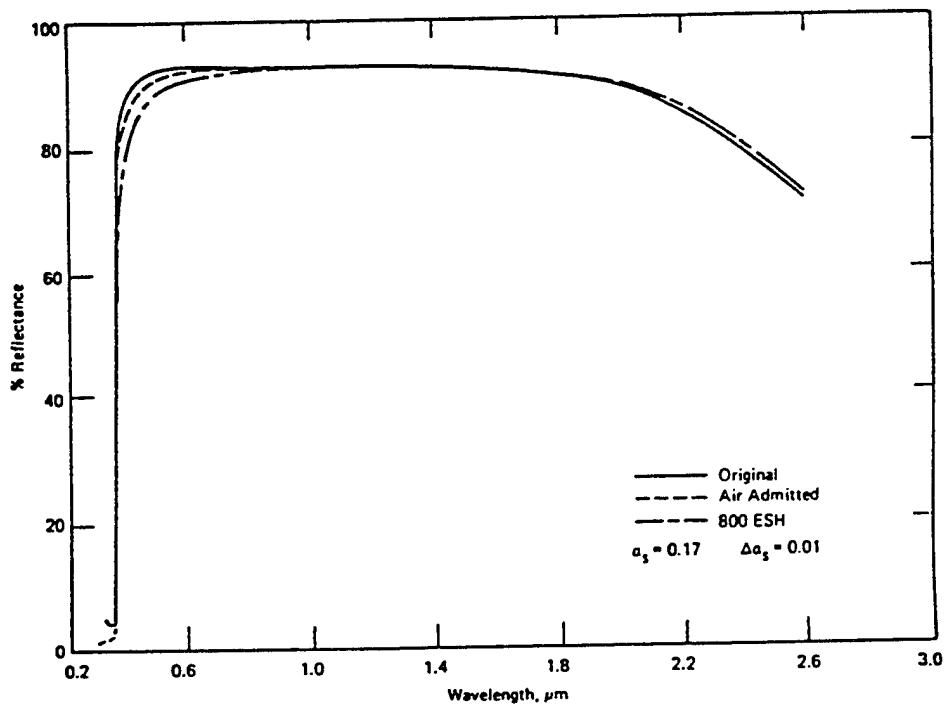


Figure 3. UV Degradation of Z93.

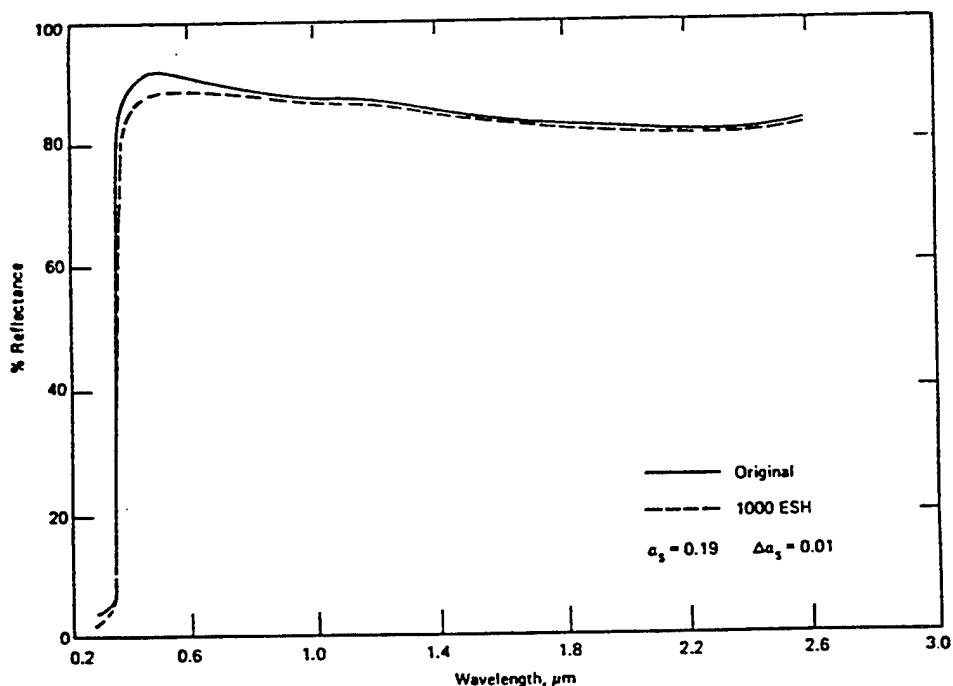


Figure 4. UV Degradation of Silicate-treated ZnO.

and then extracted and dried as a new, treated ZnO pigment. It was shown that a ZnO powder treated (reactively encapsulated) in this way does not exhibit infrared degradation. The reflectance spectra of an irradiated silicate-treated ZnO specimen are presented in Figure 4.

2.3.2 S13G/LO

The deleterious effect of outgassing, i.e., volatilization of degradable components from spacecraft surfaces which would condense on critical areas such as optics, was recognized in the early 70's. Criteria were established by NASA for an outgassing test involving exposure of the test material for 24 hours to 125°C at a pressure of less than 10^{-6} torr. The sample is weighed before and after the test to determine total weight loss (TWL). The volatile condensable material (VCM) is determined from the amount of material condensing on a collector plate maintained at 25°C, (NASA SP-R-0022A, ASTM E-595).

It was determined that the standard production batch S13G was marginal in meeting the 1.0% TWL and 0.1% VCM specified by NASA. Studies were conducted to develop improved stripping procedures for the RTV 602. Molecular distillation to remove low molecular weight components was found to be an effective means of obtaining the desired minimal outgassing characteristics. The result of these studies was S13G/LO.

2.3.3 S13G/LO-1

The removal of RTV 602 silicone from the marketplace in the early 80's necessitated development of yet another S13 material to take its place. Studies were conducted with the objective of developing a clone so that users of S13G/LO would have available a material which would not seriously affect or change design criteria. The data in Figure 5 show that the current generation S13G/LO-1 is somewhat more reflective and slightly more stable than its predecessor.

2.4 SPACE ENVIRONMENT EFFECTS

In considering the characteristics of the coatings listed in Table 3, it is apparent that the particular mission demands will determine which system should be used. For near-earth orbital flights of relatively short duration or for use on thin, flexible substrates, a silicone system such

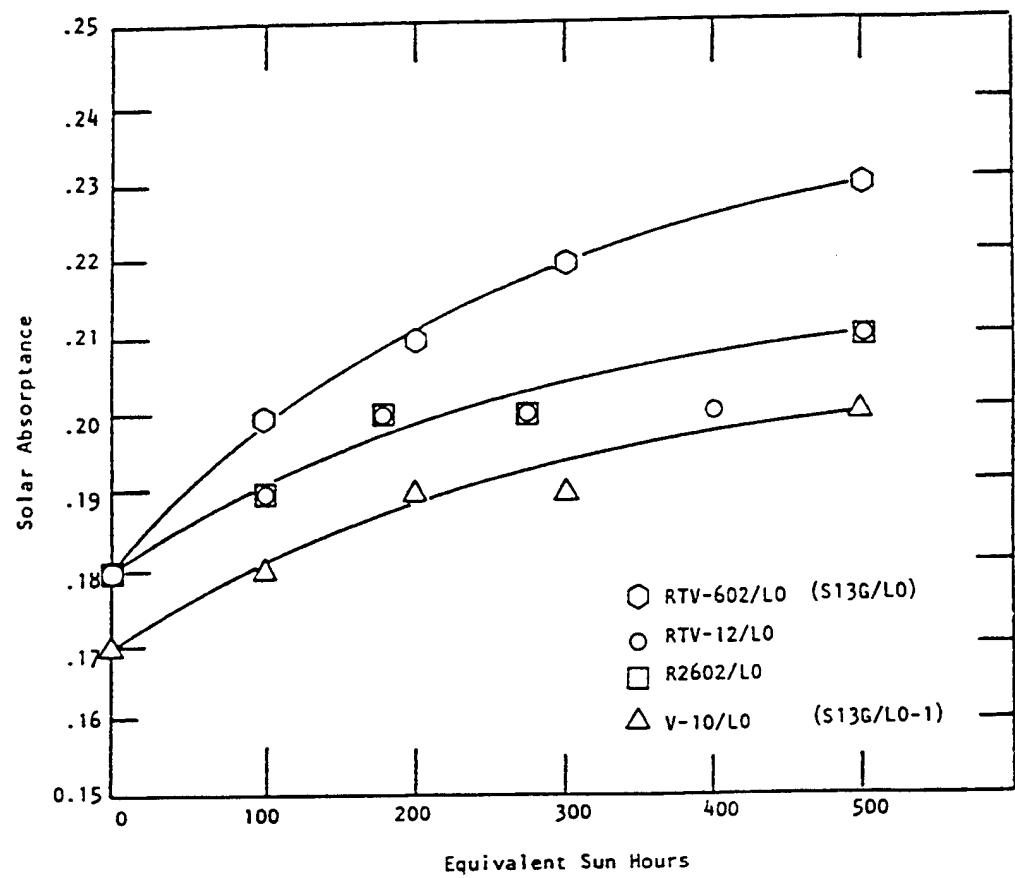


Figure 5. Solar Absorptance vs. Equivalent Sun Hours
for Different Resin Systems.

as IITRI's S13G/LO-1 has been used extensively. For missions of longer periods and where stability to particulate radiation as well as UV is critical, inorganic systems have been specified.

The optical properties and the response of our solar reflector coatings to space environmental factors are presented in Table 4. A 5000 ESH test conducted at NASA/Marshall Space Flight Center has been our most extended laboratory test on these coatings. The results for this test presented in Table 5 reveal a change in solar absorptance of about 0.02 for the YB-71 samples. In the same test, Z93 exhibited a $\Delta\alpha_s$ of about 0.03, and S13G/LO a change of 0.06. In all cases, emittance was not affected by UV-vacuum.

TABLE 4. SOLAR REFLECTORS: THERMO-OPTICAL PROPERTIES

	Z93	S13G/LO-1	YB-71 (ZOT)
Composition	ZnO-potassium silicate	ZnO (encapsulated)-methyl silicone	Zn ₂ TiO ₄ -potassium silicate
Solar Absorptance	0.15	0.18	0.12
Total Normal Emittance	0.90	0.90	0.90
$\Delta\alpha_s$, 5000 ESH	0.03	0.10	0.02
Thermal Shock Resistance	Good	Good	Good
Atomic Oxygen Resistance	Good	Good	Good
Outgassing: TML VCM	1.5% 0	0.2% 0.02%	1.5% 0
Temperature Capability	700°C	300°C	900°C

**TABLE 5. CHANGES IN SOLAR ABSORPTANCE AND EMITTANCE
AFTER 5000 ESH EXPOSURE^(Ref.4)**

Sample	Solar Absorptance, α_s			Emittance, ϵ_T	
	Initial	After 5000 ESH	$\Delta\alpha_s$	Initial	After 5000 ESH
YB-71 (1112)	.149	.166	.017	.907	.905
YB-71 (185)	.131	.151	.020	.885	.884
YB-71 (205)	.155	.166	.011	.893	.890
YB-71 (190A)	.174	.193	.019	.896	.894
YB-71 (LH112)	.122	.145	.023	.890	.888
Z93	.174	.202	.028	.896	.895
S13G/LO	.184	.245	.061	.901	.900

Long-term data for YB-71 has been generated in a geosynchronous orbit (GEO) flight experiment.⁶ Solar absorptance data determined from calorimetric measurements for the ZOT coatings on aluminum revealed the following optical behavior:

Days After Launch	α_s	$\Delta\alpha_s$
0	0.19	
400	0.26	0.07
800	0.30	0.11
1200	0.31	0.12
1600	0.32	0.13

A mirror sample on this same calorimeter experiment showed minimal $\Delta\alpha_s$, indicating the YB-71 degradation was not due to contamination.

In comparison, much stronger degradation of $\Delta\alpha_s = 0.26$ has been observed for S13G/LO from NAVSTAR 6 after about 3 years in GEO. Current technology indicates an initial α_s of ≤ 0.12 for YB-71. Based on comparable rates of solar absorptance degradation observed for different ZOT samples, a lower terminal α_s of ≤ 0.30 may be anticipated after an extended period in GEO.

Low earth orbit (LEO) altitudes are considered to lie within the range of 200 to 600 km. At these altitudes, the major atmospheric constituent is atomic oxygen (AO) which occurs as a result of UV dissociation of molecular oxygen, and which attacks a variety of materials through both oxidation and erosion processes. Coatings have been flown on short term shuttle flights, and S13G/LO and YB-71 have been shown to be resistant to AO, exhibiting no change in α_s or ϵ^7 . A compilation of AO effects on materials was reported by Banks et al.⁸ at a NASA/SDIO workshop. The data for YB-71 and S13G/LO were as follows:

Coating	Erosion Yield,		
	$\times 10^{-24} \text{ cm}^3/\text{atom}$	$\Delta\alpha_s$	$\Delta\epsilon$
YB-71	00	0.005	0
S13G/LO	00	-0.005	0

The compositional makeup of the silicate and silicone materials may be such that oxygen needs are satisfied, obviating any oxidation effects.

Contamination, both molecular and particulate, has caused degradation in both optical and thermal control systems. Outgassing tests based on ASTM E-595 have been conducted on the three IITRI coatings by Ball Aerospace and Nusil. The results for TML (total mass loss) and VCM (volatile condensable material) have been on the average 0.2% TML and 0.02% VCM for S13G/LO-1 which are well within the NASA criteria of 1.0%/0.1%. No VCM is observed for the water-based inorganic coatings, even though the TML is above 1%. This small amount of water would be purged away quickly by the vacuum of space, and the inorganic coatings can be considered nonoutgassing for long-term mission requirements.

2.4 RESULTS FROM LDEF EXPERIMENTS

The recovery of the Long Duration Exposure Facility (LDEF) and its experimental packages have enhanced our knowledge of the long-term performance of materials and systems in the natural and induced space environment. The LDEF mission provided over 5½ years of space exposure for its 57 experiments. The Thermal Control Surfaces Experiment (TCSE), S0069/DRWilkes, was perhaps the most complex experiment on the LDEF and was designed

to study the effects of the space environment on thermal control surfaces.⁹ The TCSE combined in-space spectral reflectance measurements of test materials with extensive pre- and post-flight analyses to study these effects.

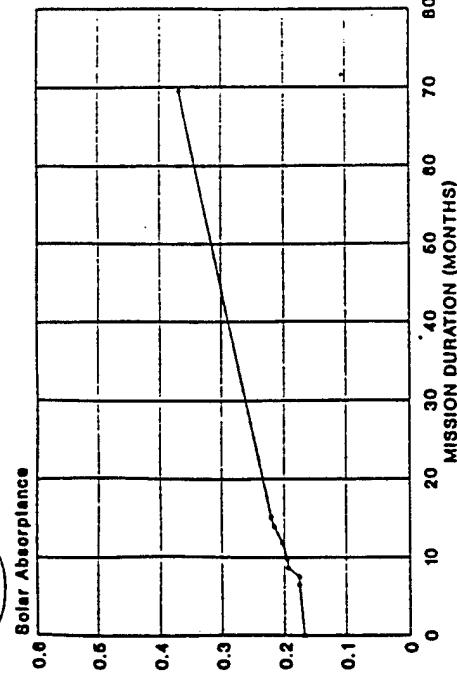
Some observations can be made from the detailed LDEF/TCSE inspections and initial post-flight thermo-optical measurements of the TCSE samples. The individual effects as well as the combined effects of the atomic oxygen, solar UV, thermal vacuum, micrometeoroid/debris, and contamination are apparent on the LDEF and TCSE surfaces. Some surfaces showed discoloration due to contamination and solar UV exposure while others showed a lack of expected discoloration, apparently due to the scrubbing effect of atomic oxygen. The texturing and erosion effects of the ambient atomic oxygen is apparent on polymeric materials such as FEP Teflon.

The TCSE flight sample array included three IITRI white coatings--S13G/LO, Z93, and YB-71 (Figure 6). The S13G/LO white paint did degrade, as expected, in the almost 6-year space exposure. However, this degradation of the solar absorptance was significantly greater than was predicted from ground simulation testing. The inorganic coatings, Z93 and YB-71, were very stable for the LDEF/TCSE mission with almost no change in thermo-optical properties. Similar behavior for IITRI coatings was observed in other LDEF experiments.¹⁰⁻¹²

The LDEF/TCSE results show that there are white coatings which are stable in the low earth orbit space environment. The available materials are limited and new materials and coatings will be required to meet the challenges for future space missions. Experiments like the LDEF and the TCSE must continue to be flown to better characterize the performance of current and new materials for different environments and mission durations.

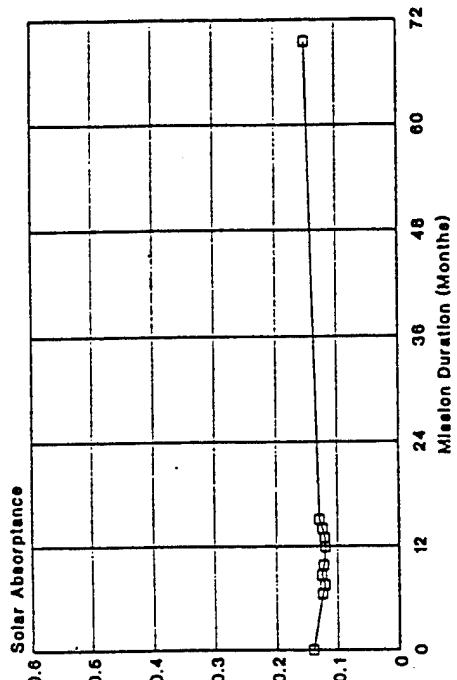
LDEF THERMAL CONTROL SURFACES EXPERIMENT
S13G/LO White Paint - Sample C92

(AZ_{Tm})



LDEF Thermal Control Surfaces Experiment
Z93 White Paint - Sample C95

(AZ_{Tm})



LDEF Thermal Control Surfaces Experiment
YB71 over Z93 - Sample C93

(AZ_{Tm})

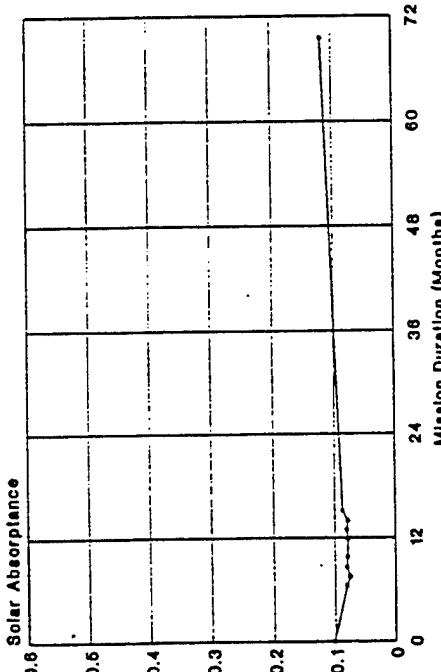


Figure 6. Long Duration Exposure Facility Thermal Control Surface Experiment.

3. RESULTS AND DISCUSSION

3.1 MATERIALS SELECTION AND ACQUISITION

The identification of the potassium silicate solution which would be a viable candidate to replace Sylvania's PS7 was the primary activity in the initial phase of this program. Alternate companies considered as sources for alkali silicates were PQ Corporation (Philadelphia, PA) and Zaclon Industries Inc. (Cleveland, OH). A listing of Zaclon's potassium silicate products in 1991 is shown in Table 6. The material thought to be most applicable as a replacement for PS7 was their Electronics No. 200. Communication with Zaclon at the inception of this program indicated: (1) a very limited market; and (2) no commitment as to its continued production. Recent inquiries as of this writing have revealed that the material is now listed as Zacsil 200 and is the only potassium silicate being sold by Zaclon.

PQ Corporation's list of potassium silicates in their 1988 catalog is shown in Table 5. Also shown in Table 7 are the specifications for PS7. Their list (Schedule No. SS91403) of December 1, 1991, shows a decrease in available materials to Kasil-1, Kasil-6, and Kasil-2130. These were the candidate silicate binders for this program. A verbal commitment as to the continued availability of these materials was obtained from M. Vincent of PQ. A Product Specification and Certificate of Analysis for Kasil-2130 are shown in Tables 8 and 9, and in Tables 10 and 11 for Kasil-1.

3.1.1 Evaluation of Potassium Silicate Binders

The PS7 and Kasil 2130 materials were analyzed for the following properties:

1. Solids content;
2. Trace impurities;
3. Potassium and silicon content; and
4. pH.

The results of gravimetric studies to determine solids content in the different solutions are shown in Table 12. Evaporating to dryness at room temperature produced glassy appearing solids which apparently still contained water. Drying at 40°C over extended times up to 17 days removed more water. Finally, all samples kept at 100°C for 24 hrs revealed solids content which were about 3% higher, or close to the manufacturer's designations. It is possible that this

TABLE 6. SPECIFICATIONS AND TYPICAL PROPERTIES*
ZACLON POTASSIUM SILICATES, TECHNICAL

Property	Water Solutions			Solid Glass Flakes	
	No. 30	No. 200	No. 805	No. 30	No. 865
Appearance	Turbid liquid	Filtered, clear water-white	Filtered, clear water-white	Glass-like plates	Glass-like plates
Wt. ratio, SiO ₂ /K ₂ O	2.50 ± 0.05	2.07 ± 0.03	2.10 ± 0.05	2.50 (2.45-2.58)	2.19 (2.10-2.25)
Mole ratio, SiO ₂ /K ₂ O SiO ₂ content, wt%	3.92 20.00 ± 0.50	3.25 19.50 ± 0.30	3.33 26.25 ± 0.50	3.95 71.0 (27.8-29.0)	3.44 68.30 67.2 min
K ₂ O content, wt%	0.30 ± 0.20	0.42 ± 0.14	12.45 ± 0.20	20.4 (27.8-29.0)	31.20 30.50 min
Specific Gravity, 60 F (16 C) degrees Baumé	30.2 ± 0.20	30.4 ± 0.20	40.5 ± 0.25	-	-
Bulk density, 60 F (16 C), lb/gal (kg/m ³) (as filled), lb/ft ³ (kg/m ³)	10.5 (1250)	10.6 (1270)	11.6 (1350)	70 (1121)	73 (1169)
Viscosity, 77 F (25 C) cP (mPa.s)	30	5	325	-	-
Screen Size (U.S. Screen)				- 80 mesh < 10% - 200 mesh < 1%	- 80 mesh < 10% - 200 mesh < 1%

*This table contains properties based on historical production performance. Zaclon does not make any express or implied warranty that all future production will demonstrate or continue to possess these typical properties.

TABLE 7. TYPICAL COMPOSITION AND PROPERTIES OF LIQUID KASIL® POTASSIUM SILICATES

		All Values Determined @ 68°F (20°C)							
		Density			Viscosity Centipoises			pH	Characteristics
Mole Ratio (SiO ₂ /K ₂ O)	Wt. Ratio (SiO ₂ ,K ₂ O)	Wt. % K ₂ O	Wt. % SiO ₂	°Bé	lb/gal	g/cm ³			
KASIL Liquids - Standard Grades									
KASIL® #1	3.92	2.50	0.30	20.0	10.5	1.26	40	11.3	Clear liquid
KASIL® 33	3.29	2.10	11.6	37.3	11.2	1.34	430	11.7	Clear liquid
KASIL® #6	3.29	2.10	12.65	40.3	10.3	1.38	1060	11.7	Clear liquid
KASIL Liquids - Electronic Grades									
Kasil® 2130	3.30	2.10	9.5	20.0	-	10.6	1.27	-	Very clear, low viscosity
Kasil® 2135	3.30	2.18	11.0	24.0	-	11.0	1.33	-	Very clear, high solids
Kasil® 1624	2.50	1.65	9.1	15.0	-	10.15	1.22	-	Very clear

TABLE 8. PRODUCT SPECIFICATION - KASIL® 2130

THE PQ CORPORATION
PRODUCT SPECIFICATION

PRODUCT: KASIL® 2130

DESCRIPTION: A 2:1 ratio potassium silicate.

Properties	Limits	PQAP*
K ₂ O, %	9.45 to 9.61	004
SiO ₂ , %	19.80 to 20.14	006
Ratio %SiO ₂ /%K ₂ O	2.06 to 2.13	Calculation
°Baume at 20°C	30.6 to 31.2	025
Total Solids, %	29.25 to 29.75	Calculation
Fe, ppm	30 (max.)	AA/ICP
Cu, ppm	0.5 (max.)	AA/ICP
Ni, ppm	0.3 (max.)	AA/ICP

Appearance: Nearly clear colorless solution.

*PQAP = PQ Analytical Procedure

TABLE 9. PQ CORPORATION CERTIFICATION



Front & Lamont Streets
P.O. Box 200
Chester, PA 19016
(215) 447-3900

2/10/92

IIT RESEARCH INSTITUTE
3441 SOUTH FEDERAL STREET
CHICAGO, ILL 60616

ATTN: Y. HARADA

THIS IS TO CERTIFY THAT THE MATERIAL SHIPPED 2/10/92

AGAINST YOUR PURCHASE ORDER NUMBER 22811

MEETS OUR SPECIFICATION.

THE ANALYSIS IS AS FOLLOWS:

1 NED 55
KASIL #2130

LOT # C11491

ALKALI:

9.60%

SIO₂:

20.11%

RATIO:

1:2.095

GRAVITY:

31.215

VISCOSITY:

(IF APPLICABLE)

SINCERLY,

Joseph R. Cardella Jr.
JOSEPH R. CARDELLA, JR.
SENIOR OPERATIONS ASSISTANT

TABLE 10. PRODUCT SPECIFICATION - KASIL® 1

THE PQ CORPORATION
PRODUCT SPECIFICATION

PRODUCT: KASIL® 1

DESCRIPTION: A 2.5 ratio potassium silicate of approximately 10.5 pounds per gallon density and 40 cps viscosity.

Properties	Limits	PQAP*
K ₂ O, %	8.30 ± 0.20	004
SiO ₂ , %	20.75 (Typical)	006
Ratio, %SiO ₂ /%K ₂ O	2.5 (Typical)	Calculation
°Beume, at 20°C	29.8 ± 0.3	025
Viscosity @ 20°C	40 cps (Typical)	023

Appearance: Clear to opalescent liquid.

*PQAP = PQ Analytical Procedure

TABLE 11. CERTIFICATE OF ANALYSIS



Front & Lamokin Streets
P.O. Box 200
Chester, PA 19016
(215) 447-3900

CERTIFICATE OF ANALYSIS

CUSTOMER:	ECCELESTONE IND.	P.O. NUMBER:	22745
PRODUCT:	KASIL#1	DATE OF SHIPMENT:	12/06/91
LOT NUMBER:	120991	TT / TC NUMBER:	16817/21253
		BILL OF LADING:	411881

I certify that this material meets all the requirements of the PQ Corporation Sales Specifications.

TEST	VALUE	UNITS
K2O	3.38	Percent
SiO2	29.73	Percent
Ratio	2.480	% K2O / % SiO2
Gravity	29.99	Degree Braine
Viscosity	NA	CPS
	NA	SS
Solids	29.98	Percent
Temperature	50	Degrees F

Analyst: JOSEPH CARDELLA

Signed: Joseph Cardella
The PQ Corporation
FOOT OF LAMOKIN ST.
CHESTER, PA., 19013
(215)-447-3900

TABLE 12. SOLIDS CONTENT OF CANDIDATE PQ POTASSIUM SILICATES AND PS7

Time (Days)	Sol Behavior (% Solids)						Remarks	
	PS7 (35%)		Kasil 2130 (29.1%)		Kasil-1 (29%)			
	#5381-B2	R&D*	ICD*	R&D*	ICD*			
(A) Drying at Room Temperature in Ambient Humidity Conditions								
8	43.45	35.94	37.62	37.28	36.66	All samples stayed clear.		
14	43.35	35.90	37.43	37.26	36.58			
(B) Drying at 40°C in Oven								
1	43.42	35.88	37.23	36.72	37.73	Only Kasil-1 sample stayed clear.		
4	41.73	34.73	35.99	35.16	35.37			
8	41.23	34.32	35.60	33.98	34.58			
17	40.28	33.65	34.72	33.22	33.76			
(C) Samples from (B) Kept at 100°C for 24 Hours								
1	37.64	31.81	32.70	32.61	32.99	None stayed clear.		

* R&D - PQ Corporation Research and Development; ICD - PQ Industrial Chemicals Division.

3% may be due to physically or chemically combined water which could be driven off at higher temperature and/or longer times.

The silicate materials were analyzed* using Optical Emission Spectroscopy (OES). The results shown in Table 13 reveal very small amounts of trace impurities for both PS7 and Kasil 2130, and the two to be of essentially equivalent purity. However, the results for potassium and silicon were suspect in that the results show $\text{SiO}_2:\text{K}_2\text{O}$ ratios of 0.82 and 1.40, respectively, for PS7 and Kasil 2130; these are significantly different than the supplier spec of a 2.10 ratio. OES analyses of Kasil 2130 by a laboratory in the Chicago area produced values of 1.50 and 1.46 which also appeared to be erroneous. These results indicate that OES is not a good test for the major K and Si components in potassium silicate solutions.

Communication with PQ Corporation revealed that they had developed titration analytical methods for K and Si in potassium silicate. Analytical methodology obtained from PQ Corporation were used in the determination of the percent alkali and silicate contents which meets PQ current material specifications. The results shown in Table 14 were obtained using methods PQAP [10/16/78] and PQAP 006A [12/19/78], provided by the PQ Corporation, Research and Development Center through Ms. Joan Isaacs. For the analyses, the samples were dispensed into LDLPE labware and titrated to the appropriate endpoint, depending on the species of interest (i.e., K_2O or SiO_2).

The titration data in Table 14 show that all of the solutions contained amounts of SiO_2 and K_2O which were quite close to those designated by the suppliers, i.e., 23.9 wt% SiO_2 and 11.4 wt% K_2O for Sylvania's PS7, and 20.0 wt% SiO_2 and 9.5 wt% SiO_2 for PQ's Kasil 2130. Additionally, the $\text{SiO}_2/\text{K}_2\text{O}$ wt ratio of ~2.10 was approached by all of the samples as determined by our titration and as certified by the suppliers. Thus, the ratio of silica to potassium oxide is similar for PS7 and Kasil 2130, although the actual solids content differ: ~35.3% for PS7 and ~29.5% for Kasil 2130.

*Analyses were obtained by M. Meshishnek, Aerospace Corporation.

TABLE 13. QUANTITATIVE ANALYSIS OF POTASSIUM SILICATES

	PS7	Kasil 2130
Si	9.2%	11%
K	20	14
Mg	0.00035	0.00079
Fe	0.0079	0.0079
Al	0.0024	0.0047
V	0.0030	0.0012
Cu	0.00025	0.00018
Na	0.048	0.051
Ti	0.0032	0.0051
Ca	0.011	0.00093
B	ND < 0.002	ND < 0.002
Li	ND < 0.002	ND < 0.001
Other Elements	nil	nil

TABLE 14. RESULTS OF TITRATION ANALYSES FOR PS7 AND KASIL 2130

Material	Run No.	Wt % SiO ₂	Wt % SiO ₂	Wt Ratio, SiO ₂ /K ₂ O	Supplier COA*		Wt Ratio SiO ₂ /K ₂ O
					% SiO ₂	% K ₂	
PS7 (Lot #5381B2)	1	23.14	11.31	2.05	23.73	11.21	2.12
	2	23.26	11.30				
Kasil 2130 (Lot #C11491)	1	19.53	9.62	2.04	19.98	9.61	2.08
	2	19.80	9.63				
Kasil 2130 (Lot #C061894)	1	20.27	9.60	2.11	20.11	9.53	2.11

*COA - Certificate of Analysis

The difference in solids content between PS7 and Kasil 2130 had no significant effect in the pH of the as-received solutions as shown in Table 15. The addition of de-ionized water to these solutions to simulate actual compositions used for paint formulations resulted in a small drop in pH. However, the diluted PS7 and 2130 solutions exhibited values which were quite close.

In summary, these analyses show that Kasil 2130 is chemically quite similar to PS7.

3.1.2 Pigment Materials

The basic pigment for Z93 and for S13G/LO-1 is SP500 zinc oxide which is obtained from Zinc Corporation of America. A representative chemical analysis of this material is shown in Table 16. Production limits are 5, 8 and 1 ppm for CdO, PbO and Fe₂O₃. New Jersey Zinc Co., Inc. was the predecessor to Zinc Corporation of America, the current producer of SP500 ZnO. The SP500 is processed at IITRI by a 625°C/16 hr heat treatment for use in Z93, and by a potassium silicate encapsulation process for incorporation into S13G/LO-1.

TABLE 15. pH OF POTASSIUM SILICATE SOLUTIONS

Trademark	As-Received Solution	Z93 or Z93P Binder Solution	YB-71 or YB-71P Binder Solution
PS7	11.85	11.60	11.76
Kasil 2130 (11491)	11.81	11.56	11.74
Kasil 2130 (C061894)	11.78	11.58	11.72

The zinc orthotitanate (ZOT) pigment for YB-71 is produced in IITRI's laboratories by the synthesis process shown in Table 17. As part of this program, ZOT has been evaluated using XRD analysis, SEM characterization, and optical spectral measurements. Several different ZOT powder samples were submitted to Dr. Michael Meshishnek, Aerospace Corporation, for

TABLE 16. NJZ TECHNICAL INFORMATION

**NJZ
technical
information**

No.
Date:

S. P. ZINC OXIDE - 500

"Super Purity"

Highest purity zinc oxide in the form of extremely fine white powder

Chemical Properties (representative analysis)

ZnO (freshly ignited)	99.99 %	- CdO0002%
SO ₃ (Total S as)002	- Al	<.001
Fe0001	- Ca	<.001
Cu	<.0001	- Na	<.001
Mn	<.0001	- Si	<.0005
PbO0006	- Mg	<.0004
As ₂ O ₃	<.00001	-	

Physical Properties

Specific Gravity	:	5.6	(1 lb. bulk .0214 gals.)
Specific Surface (S)	:	3.6 - 2.7	Square Meters/gram
Surface Mean Diameter	:	.30 - .40	microns

Uses

S. P. 500 Zinc Oxide is suggested for use where a zinc material in the form of an oxide of extremely high purity is desired.

NJZ The New Jersey Zinc Company, Inc.
Palmerton, Pennsylvania 18071



The information herein has been compiled from sources which we believe to be reliable, but we assume no responsibility or liability for its accuracy or for the result of any application made of any information contained herein, nor do we assume any liability for infringement of any patent which may result from the application of such information.

evaluation. These samples were all prepared over the last 10 years as 2-lb batches by the process described in Table 17.

The results of optical emission spectroscopy shown in Table 18 indicate a high level of purity for all of the powders. Synthesis dates are shown in parentheses. The values for the major components, Zn and Ti, would appear suspect since the theoretical values are 53.9% Zn and 19.7% Ti. However, the trace element analyses suggest that a consistent high purity has been maintained in the synthesis of ZOT over the last 10 years.

TABLE 17. MIXED OXALATE (MOX) PROCESS FOR SYNTHESIS OF ZINC ORTHOTITANATE

Material Preparation	Prepare aqueous solutions of $TiCl_2$ ($< 15^\circ C$) and $ZnCl_2$ (room temperature)
Oxalate Preparation	$ZnCl_2$ (aq.) + $H_2(C_2O_4) \cdot 2H_2O$ (aq.) $\rightarrow ZnC_2O_4 \cdot 2H_2O$ (s) + 2HCl (aq.) (room temperature/1 hr)
	$TiCl_4$ (aq.) + $H_2(C_2O_4) \cdot 2H_2O$ (aq.) \rightarrow "TiOX" (s) + nHCl (aq.) (90°C/1 hr)
	Each oxalate filtered with copious water washings to pH ≈ 7 and dried at 60°-70°C for > 16 hr
Mixing	Oxalate mixtures to yield 2Zn/1Ti ratio, ball milled in nylon bottles with porcelain balls for > 10 hr
Precalcination	$ZnC_2O_4 \cdot 2H_2O$ + "TiOX" $\rightarrow Zn_2TiO_4$ + ZnO + TiO_2 + volatiles (600°C/2 hr, time to 600°C ~ 1 hr)
Flash Calcination	Zn_2TiO_4 + ZnO + TiO_2 $\rightarrow Zn_2TiO_4$ (900°C/4 hr, reaction goes to completion.) Insert directly into furnace at 900°C. Time to 900°C about 15-20 minutes. Soak for 4 hr. Remove and cool.

**TABLE 18. SEMIQUANTITATIVE ANALYSIS OF
ZINC ORTHOTITANATE POWDERS**

	ZOT-1 (Batch 933942A, 3/92)	ZOT-2 (Batch 93942B, 3/92)	ZOT-3 (Batch 86366A, 12/88)
Zn	81 %	75 %	66 %
Ti	14	8.5	9.2
Mg	0.0012	0.00056	0.00036
Si	0.0054	0.0018	TR <0.001
Cu	TR <0.00005	ND <0.00005	ND <0.00005
Al	0.0073	ND <0.001	ND <0.001
Ca	0.0062	0.0025	0.0023
Other Elements	nil	nil	nil
	ZOT-4 (Batch 86366B, 12/88)	ZOT-5 (Batch 89902A, 3/89)	ZOT-6 (Batch 89902B, 3/89)
Zn	70 %	61 %	60 %
Ti	14	11	18
Mg	0.00020	0.00037	0.00049
Si	TR <0.001	ND <0.001	TR <0.001
Cu	ND <0.00005	0.00026	0.00013
Al	ND <0.001	TR <0.001	TR <0.001
Ca	0.0016	0.019	0.0027
Other Elements	nil	nil	nil

**TABLE 18. SEMIQUANTITATIVE ANALYSIS OF
ZINC ORTHOTITANATE POWDERS (CONTINUED)**

	ZOT-7 (Batch 875788B, 2/89)	ZOT-8 (Batch 59902A, 9/87)	ZOT-9 (Batch 76366A, 7/88)
Zn	57. %	65. %	65. %
Ti	19.	26.	9.5
Mg	0.00043	0.0011	0.00040
Si	0.0032	0.0094	ND <0.001
Cu	ND <0.00004	ND <0.00005	TR <0.00005
Al	ND <0.001	ND <0.001	ND <0.001
Ca	0.0031	0.0059	0.0026
Other Elements	nil	nil	nil
	ZOT-10 (Batch 54142, 7/86)	ZOT-11 (Batch 51518, 8/83)	ZOT-12 (Batch 73538A, 5/88)
Zn	55. %	62. %	61. %
Ti	17.	18.	13.
Mg	0.00065	0.0012	0.00070
Si	ND <0.001	ND <0.001	ND <0.001
Cu	ND <0.00005	TR <0.00005	TR <0.00005
Al	ND <0.001	0.0096	0.0062
Ca	0.0013	0.0029	0.0034
Other Elements	nil	nil	nil

These 12 samples were also examined using XRD techniques. All samples were primarily cubic α Zn_2TiO_4 with small, <1% quantities of ZnO. A very small amount of $ZnTiO_3$ was detected in one sample. No titania was detected in these analyses.

3.2 REFORMULATION STUDIES

A primary consideration in the requalification program was to develop coating formulations which are as similar as possible to the coating compositions incorporating PS7. The "cloning" was to encompass all aspects from spraying behavior to physical, mechanical and optical properties of cured coatings. The ultimate goal was to develop Z93, YB-71, and S13G/LO-1 coatings containing a substitute potassium silicate with equivalent or improved stability to a space environment. The designation chosen for the newly developed materials was to simply add a "P" for ease of identification, i.e., Z93P, YB-71P, and S13GP/LO-1.

3.2.1 Z93

The traditional compositional makeup for Z93 is as follows:

300 grams of calcined SP500 ZnO
150 cc (200 grams) PS7
150 cc (150 grams) distilled water

This represents a 4.30/1 pigment-to-binder (PBR) by weight ratio in its cured state. It has been supplied commercially in a two-part kit form: Part A, pigment, and Part B, binder. The binder portion combines both the 150 cc of PS7 with 225 cc of water. The additional 75 cc water is to provide a fluidity to the formulation which is favorable for spraying of larger surface areas. However, in the cured state, the PBR of 4.30/1 is maintained.

The early studies in this program were conducted maintaining this PBR (4.30/1) and using a water content which was the same amount as the potassium silicate. Representative compositions involving the three candidate silicates, Kasil-1, 6 and 2130, were formulated and evaluated as presented in Table 19. As shown, there was a need to balance the amount of water addition to achieve the desired viscosity or sprayability.

Formulations with water content adjusted to be the same as the PS7 formulation were prepared and studied. The final reformulations and their behavior are summarized in Table 20. Based on these results, Kasil 6 was eliminated from additional studies due to the fact that its high

TABLE 19. SUMMARY OF Z93 REFORMULATION EXPERIMENTS (R-003 to R-005)

Z-93 Equivalent Experimental Candidate Formulation	Potassium Silicate Solution Used	Formulation PBR = 4.3/1	Observations
R-003	PQ-2130 30.0% (w) solids Viscosity* = 11.0 sec 1.27 gm/cc $\text{SiO}_2/\text{K}_2\text{O}$ (Wt ratio) = 2.10 (Mole ratio) = 3.30	ZnO = 300 gms 2130 = 184 cc H_2O = 184 cc	Viscosity* = 11.5 sec, density = 14.03 lb/gal. This is a thinner formulation compared to the original Z-93. Excess spray setting caused running. Formulation settles during spraying. For good spray consistency need 13 to 17.0 sec (Ford Cup 4) viscosity. Formulation can be sprayed successfully on small samples. For larger areas, longer times are needed between spray passes. For next experimental formulation, adjust H_2O to original Z-93 water content, i.e., 117 cc.
R-004	Kasil-1 29.1% (w) solids Viscosity* = 19.0 sec 1.27 gm/cc $\text{SiO}_2/\text{K}_2\text{O}$ (Wt ratio) = 2.50 (Mole ratio) = 3.92	ZnO = 300 gms Kasil-1 = 189 cc H_2O = 189 cc	Viscosity* = 11.5 sec, density = 13.94 lb/gal. This also is a thinner formulation compared to the original Z-93. Formulation settles while spraying. Spray experience same as R-003. For next experimental formulation, adjust H_2O to original Z-93 water content, i.e., 110 cc.
R-005	Kasil-6 39.2% (w) solids Viscosity* = > 11.0 min 1.39 gm/cc $\text{SiO}_2/\text{K}_2\text{O}$ (Wt ratio) = 2.10 (Mole ratio) = 3.29	ZnO = 300 gms Kasil-6 = 129 cc H_2O = 129 cc	Viscosity* = 15.5 sec, density = 16.24 lb/gal. This is a thick formulation compared to original Z-93. Sprays satisfactorily but thinning may improve sprayability along with less chance of gun clogging. For next experimental formulation, adjust H_2O to original Z-93 water content, i.e., use 172 cc.

*Viscosity = Viscosity measured by Ford Cup No. 4.

TABLE 20. SUMMARY OF REFORMULATION EFFORTS (R016 TO R018)

Z-93 Equivalent Experimental Candidate Formulation	Potassium Silicate Solution Used	Formulation PBR = 4.31	Observations	Remarks
R-016 (following R-006)	PQ-2130 30% (w) solids Viscosity* = 11.0 sec $\text{SiO}_2/\text{K}_2\text{O} = 2.10$ (wt ratio) = 3.30 (mol ratio)	ZnO = 300 gms 2130 = 184 cc H ₂ O = 117 cc	Viscosity* = 13.2 sec; density = 15.4 lb/gal. Sprays well, no appreciable settling, no streaking or running. Overnight prime-cure, passes hot-water test.** Cure-adhesion satisfactory. Passes tape-peel test after complete cure of 7 days.	This formulation to be used for optical and mechanical response characterization.
R-017	Kasil-6 39.2% (w) solids Viscosity* >9.0 min. $\text{SiO}_2/\text{K}_2\text{O} = 2.10$ (wt ratio) = 3.29 (mol ratio)	ZnO = 300 gms Kasil-6 = 129 cc H ₂ O = 172 cc	Viscosity* = 13.0 sec, density = 15.2 lb/gal. Sprays well, but shows appreciable settling which results in streaking; >2 day curing required to pass hot water test.** Passes tape-peel test for adhesion after cure of 7 days. Two days old mixture has viscosity* - 15.1 sec implying chemical reaction between species.	Although difficulties in spraying and cure could be avoided <u>use of Kasil-6 may not be advisable</u> because of settling behavior, and observed possibility of chemical reaction indicated by increase in viscosity.
R-018	Kasil-1 29.1% (w) solids Viscosity* = 19.0 sec $\text{SiO}_2/\text{K}_2\text{O} = 2.50$ (wt ratio) = 3.92 (mol ratio)	ZnO = 300 gms Kasil-1 = 187 cc H ₂ O = 110 cc	Viscosity* = 13.2 sec, density = 14.9 lb/gal. Sprays well, slight settling, but does not result in streaking or running. Overnight cure, pass hot water test.** Passes tape-peel test for adhesion after 7 days cure. This formulation loses water faster. Sample surfaces were hard and difficult to scrape after 4 days, indicating complete cure.	This formulation to be used for further optical and mechanical response characterization.

* Viscosity measured by Ford Cup No. 4. ** Hot Water Test is a qualitative test used to evaluate adhesion of the formulated candidate coating system. The test involves priming water-break free cleaned aluminum substrates with candidate formulation of candidate solution. The primed coat is then given an 18 to 24 hrs of cure at room temperature, and then held under running hot water to examine its tenacity to the substrate. The results of this are qualitative observations of comparative cure behavior in a given time with similarly applied Z-93 (with PS-7) primer coat. If response of the test is comparable with Z-93 (with PS-7), then we consider candidate formulation "passes". If response is not comparable, we document the differences. (In case of R017, 24 hrs cure was not enough to pass the test; 2 days were required to pass the test.)

viscosity rendered it to a difficult to spray and cure material. The Kasil 2130 was of the same chemical makeup and had a lower viscosity, and this material was chosen for additional investigations. Studies involving Kasil-1 were also deemphasized due to its high brittleness as a Z93 coating. However, additional studies involving compositional modifications offers the potential to develop a Z93 (Kasil-1) having a tougher surface, and hence, cleanability.

3.2.2 YB-71

Experience gained through reformulation experiments with Z93 was helpful in establishing compositional parameters for YB-71. Samples were prepared using Kasil 2130, Kasil-1 as well as PS7. The main emphasis was on duplicating the 7.1 to 1 PBR with the ZOT pigment and Kasil 2130 as the binder material.

The optimum formulations to emerge from these early studies are shown in Table 21. Subsequent studies of adhesion behavior using a torsion test suggest a further modification in water content to achieve improved adhesion, although a slight sacrifice in surface hardness is also observed. This is elaborated on in later sections of this report.

3.2.3 S13G/LO-1

The initial development of S13G pigment as an engineering space stable pigment material was carried out at IITRI under contracts from the Jet Propulsion Laboratory (JPL) and Marshall Space Flight Center (MSFC). The details of these development studies conducted over several years have been well documented in IITRI reports IITRI-C06053¹³ and IITRI-C06062.¹⁴ An excellent summary of this work has been given by Zerlaut et al.¹⁵ Important factors governing the preparation and storage of S13G/LO thermal control material are controlled by standard operating procedures (SOPs) developed as part of the above. The following list summarizes the important factors.

1. Initial ZnO Potassium Silicate/Sol Reaction and Reaction Parameters: (i) Material mass balance parameters: sol to D.I. H₂O ratio, K/Si ratio, Zn/Si ratio and K/Zn ratio; (ii) reaction temperature; (iii) mixing parameters; (iv) heating/cooling method and related parameters; and (v) filtration method.
2. Pigment "Sweating" and Sweating Parameters: (i) Sweating seal material; and (ii) sweating time. (Sweating time controls thixotropy of pigment.)

TABLE 21. YB-71 REFORMULATION WITH KASIL 2130

YB-71 Equivalent Experimental Formulation	Potassium Silicate Solution	Formulation PBR = 7.1/1	Observations	Remarks
R-028	PQ-2130 30% (w) solid Density = 1.27 gm/cc Viscosity = 11.0 sec $\text{SiO}_2/\text{K}_2\text{O} = 2.10$ (wt ratio) $= 3.30$ (mol ratio)	ZOT = 455 gms 2130 = 169.5 cc $\text{H}_2\text{O} = 62$ cc	Viscosity* = 13.2 sec. Sprays well, no streaking or running but slight settling observed. Overnight cure passes hot water test, 7 days cured samples passed tape-peel test.	Use this formulation for further optical and mechanical response characterization.
R-053	Kasil-1 29.1% (w) solid Density = 1.27 gm/cc Viscosity = 19.0 sec $\text{SiO}_2/\text{K}_2\text{O} = 2.10$ (wt ratio) $= 3.92$ (mol ratio)	ZOT = 455 gms Kasil-1 = 171.6 cc $\text{H}_2\text{O} = 59$ cc	Viscosity* = 13.8 sec. Sprays well, no streaking or running but slight settling observed. 14 days cured samples passed tape-peel test.	Use this formulation for further optical and adhesion response characterization.

* Viscosity measured by Ford Cup No. 4.

3. Pigment "Washing": (i) Washing procedures, (ii) wash chemistry, (iii) wash time.
4. Pigment Drying and Sizing: (i) Drying temperature; (ii) drying time; and (iii) sizing procedures and means.
5. Silicone Paint Mixing Procedures: (i) Grinding procedures and grind formulation; and (ii) overall grinding time (upper limit of grinding time).
6. Shelf Life, Impact Assessment: (i) Chemical nature of S13G pigment surface.

ZnO is a fast dissolving semiconductor in high pH solutions.¹⁶ An understanding of the overall encapsulation procedure shows that processing factors 1 through 4 (listed above) determine the performance and physical and surface properties of the pigments. Processing steps 5 and 6 are affected by the microstructure and chemical properties of the pigment surface. Additional details on the preparation of S13G pigment were reported earlier by Zerlaut et al.¹⁵

3.2.3.1 Reformulation Studies and Discussion

Our approach in the reformulation studies was to use available, selected potassium silicate sols to carry out reactive encapsulation reactions. The resultant reaction products were then analyzed for their chemical and physical nature for further use as an engineering pigment.

Kasil 2130 and Kasil-1 were considered candidate sols for the reactive encapsulation. The feasibility of the reactive encapsulation was first checked via bench-scale batches in accordance with existing SOPs detailed by Zerlaut et al.¹⁵ Retains were taken at each step for gravimetric and chemical elemental analysis. The results of bench-scale reactive encapsulation experiments are presented in Table 22.

The initial bench-scale reaction batch processing was performed with PS-7 as the sol (Batch R-48). A small portion of material was purposely overcooked to characterize its chemical nature. It is our experience that the existing SOP produces a small portion of overcooked material. The results of chemical analyses are listed in Table 22 as R-48-1 and R-48-1-OC (OC - overcooked). The reaction products were wrapped in Tedlar and sweated overnight at ambient

TABLE 22. CHEMICAL COMPOSITION OF RETAIN SAMPLES TAKEN DURING REACTIVE ENCAPSULATION OF ZnO (SP-500)

Sample No.	Reactants	Measured, w/o			Calculated, w/o			Total	SiO ₂ K ₂ O w/o ratio (A)	Percentage Increase in (A) (%)	Remarks
		Zn	K	Si	ZnO	K ₂ O	SiO ₂				
R-48-1	ZnO (SP-500)	66.57	4.02	5.65	82.66	4.82	12.09	99.77	2.51	—	Retain after reactive encapsulation.
R-48-1-OC	and Kasil-2130	39.84	7.48	12.99	49.40	8.96	27.80	86.18	3.10	—	Retain of OC material after sweating.
R-48-2	PS-7	74.39	1.45	2.57	92.24	1.74	5.50	99.48	3.16	25.90	Retain after 1st wash with D.I. H ₂ O of overnight sweatied pigment.
R-49-1	ZnO (SP-500)	66.43	4.00	5.70	82.37	4.80	12.20	99.37	2.54	—	Retain after reactive encapsulation and sweating.
R-49-1	Kasil-2130	72.41	2.08	3.32	89.79	2.44	7.10	99.33	2.91	14.57	Retain after 1st wash with D.I. H ₂ O of overnight sweatied pigment.
R-50-1	ZnO (SP-500)	68.11	3.36	5.05	84.46	4.03	10.81	99.30	2.68	—	Retain after reactive encapsulation and sweating.
R-50-2	Kasil-2130	75.04	1.23	2.29	93.05	1.48	4.90	99.43	3.31	23.61	Retain after 1st wash with D.I. H ₂ O of overnight sweatied pigment.
R-50-3	Washing pigment with Na ₂ HPO ₄ Sol	75.68	0.67	2.10	93.83	0.80	4.49	99.13	5.61	69.50	1st phosphatization wash.
R-50-4		76.18	0.31	2.01	94.86	0.37	4.30	99.13	11.6	106.77	2nd phosphatization wash.

temperature. The material sweated well and showed the typical light green hue in appearance. The material was then washed once with D.I. H₂O and was analyzed as R-048-2.

The bench-scale reactive encapsulation was conducted twice with Kasil 2130 (R-049 and R-050). Batches R-049 and R-050 were processed identically as R-048. The mass balance of reactants was determined by measuring the silicate content of Kasil 2130 and calculating the amount of reactants while keeping K/Si, Zn/Si ratios constant among the reactants. The reaction temperature, time and other relevant parameters were kept unchanged. R-049 and R-050 reaction products were chemically analyzed and the results are listed in Table 22 as R-49-1 and R-50-1. Both batches sweated well. Comparison of R-48-1 with R-49-1 and R-50-1 indicate that the chemical compositions of the pigments are similar. According to Iller (1979),¹⁷ the hue of the reaction product is a function of the chemistry of the silicate sols. For a SiO₂/K₂O molar ratio \geq 3.3, the greenish hue for the reaction products is to be expected. The greenish hue is also an indicator that the SiO₂ to K₂O ratio remained constant and no leaching occurred. Vail¹⁸ suggests that when Zn compounds are added to alkali silicate sols, the reactions proceed according to the following steps:

- (1) First, the surface rearranges itself via alkali catalyzed protonation/hydrolysis. The Zn⁺⁺ ions at active sites forms acidic reaction products of hydrous zinc oxide.
- (2) The acidic hydrous reaction product interacts with K₂O:3.3SiO₂ to form colloidal silica via coagulation.
- (3) Coagulated silica interacts with alkali and hydrous oxide surface to form an amorphous coating over the oxide surface.

Vail notes that a 3.3 molar ratio is required to form a good coating over oxide surfaces. In general, potassium silicate of molar ratio lower than 3.3 cannot provide the required coating. This conclusion held true for all the compounds studied by Vail,¹⁵ e.g., compounds of Zn, Fe, Cu, Co.

The bench-scale reaction products of batch R-50, were subjected to complete wash cycles to verify response of material to leaching washes. Retains were taken and analyzed for chemical composition. The results listed in Table 23 fall within the range reported by Zerlaut et al.¹² Thus, it was decided to proceed with scaled up and full batch (50 lb pigment) studies to compare S13G production with the alternate replacement sols.

Kasil 2130 and Kasil-1 were chosen to process production scale batches of 50 lb ZnO pigment. Batches R-059, R-060 and R-061 were processed using potassium silicate sols Kasil 2130, Kasil-1 and PS-7, respectively. The process design and process controls implemented were kept unchanged. Retains were taken at each processing step from each cake of the filtering operation. This approach provided a sufficiently wide variety of samples for determination in process chemical composition. The results of chemical analyses are listed in Table 23. The pigment processed by using PS-7 potassium silicate sol is termed as S13G and the pigment from the other two sols, Kasil 2130 and Kasil-1, were designated as S13GP and S13GK, respectively. Comparison reveals that S13GP and S13G are similar in chemical composition, whereas S13GK is slightly more siliceous. The chemical similarity of pigments indicated the following additional observations.

- (1) The existing standard practice of reactively encapsulating ZnO (SP500) favor formation of Zn containing amorphous potassium glass coating of composition $ZnO:K_2O:SiO_2 \approx 1:1:1$ over the ZnO particles.
- (2) If reactive encapsulation is carried out at temperatures $> 165^{\circ}F$ (overcooked material), the Zn-containing potassium silicate amorphous glass tends to approach an amorphous glass composition of $ZnO:K_2O:SiO_2 \approx 1:1:3$.
- (3) Washing encapsulated material after sweating with D.I. H_2O leaches out K_2O causing SiO_2 to K_2O ratio to increase. The simultaneous SiO_2 leaching is not an efficient reaction.
- (4) Phosphatization of reactively encapsulated material is necessary to make the pigment surface compatible with silicones. The phosphate washes leach out both K_2O and SiO_2 , but removes K_2O with greater efficiency, thus causing SiO_2/K_2O ratio to increase.
- (5) S13GP pigment is chemically very similar to S13G. S13GK is slightly more siliceous.

TABLE 23. CHEMICAL COMPOSITION OF REACTIVELY ENCAPSULATED ZnO (SP500), S13G, S13GP, S13GK

Processing Step	S13G			S13GP			S13GK		
	K ₂ O w/o	SiO ₂ w/o	w/o Ratio SiO ₂ /K ₂ O	K ₂ O w/o	SiO ₂ w/o	w/o Ratio SiO ₂ /K ₂ O	K ₂ O w/o	SiO ₂ w/o	w/o Ratio SiO ₂ /K ₂ O
(I) Reactive Encapsulation:									
Cake 1	5.50	13.05	2.37	5.11	12.99	2.54	2.46	7.70	3.31
Cake 2	5.04	12.54	2.49	6.05	15.09	2.49	3.94	11.41	2.86
Cake 3	5.30	12.99	2.45	4.31	11.19	2.60	4.18	11.79	2.82
Cake 4	4.60	11.64	2.53	4.52	11.70	2.61	3.32	9.99	3.01
(II) Wash with D.I. (18 MΩ) Water:									
Cake 1	4.40	10.59	2.41	3.94	10.51	2.66	4.20	12.60	3.00
Cake 4	4.40	11.04	2.51	3.60	9.29	2.58	3.41	10.96	3.21
(III) Phosphatization (I):									
Cake 1	2.50	7.13	2.85	1.81	6.10	3.37	2.22	7.25	3.27
Cake 4	2.46	7.88	3.20	2.81	7.10	2.53	2.94	8.30	2.78
(IV) Phosphatization (II):									
Cake 1	2.98	6.21	2.08	1.03	5.39	5.24	1.70	5.06	2.98
Cake 4	1.14	5.35	5.57				0.90	5.70	6.33

In view of the chemical similarities, the S13GP material was used to produce two trial batches of S13GP/LO-1 by incorporating them with stripped polydimethyl-siloxane silicones. The resulting paint materials were applied to aluminum substrates to compare the performances of the two coating systems.

3.2.3.2 Processing/Shelf Life

The pigment S13GP was manufactured as a full batch 3 times (Batch Nos. R-059, S-041 and S-042) to investigate batch-to-batch variations. No significant differences were observed. Two separate paint batches were manufactured to evaluate paint properties (Batch Nos. R-055 and S-168). It was observed that the pigment does not provide any unusual difficulties in grinding, when one follows SOPs and formulations for mixing as spelled out by Zerlaut et al.¹⁵ The required dispersion of S13GP was obtained well before the upper grinding limit established for S13G, thus providing excellent consistency and ease for S13GP/LO-1. The sprayability and curing of new paint batches all showed similar behavior to that reported by Mell and Harada⁵ during development of S13G/LO-1.

Shelf life studies were carried out on S13GP/LO-1 (Batch Nos. R-055 and S-168). The pint size kits were stored below 0°F for a period of 8 to 9 months. The kits were removed from the freezer, thawed out and viscosity was measured. For batch R-055, no viscosity increase was noticed over the period of 8 months, whereas for S-168 a very slight increase of 2 sec (when measured in Ford Cup No. 4) was noticed in viscosity over the period of 9 months. This indicates that S13GP/LO-1 meets the shelf life requirements of S13G/LO-1.

3.3 COATING PROPERTIES

Sprayability and curing behavior were discussed in the previous section dealing with reformulation studies. The priming procedure for the inorganic Z93 and YB-71 was to rubprime the substrate with Z93, i.e., hand application with pressure to form a thin <1 mil film. For the silicone-based S13G/LO-1, modified silane primer materials are used, GE's SS4044 for metallic substrates, and UC's A1100 for non-metallic surfaces. Adjustments in composition and modifications in spray techniques were incorporated to optimize the physical properties of coatings, i.e., adhesion and coating integrity. The desired formulation viscosity and spray

technique, however, are the province of the particular "sprayer" or person applying the coating and these may vary to some extent. The compositions presented in Tables 20 and 21 for inorganic Z93 and YB-71 should therefore be considered a guide, and some flexibility in these parameters is probably desirable.

3.3.1 Optical Properties

Samples for optical properties determinations were submitted to AZ Technology, Huntsville, AL, early in this program. Reflectance measurements were made using an AZ Technology LPSR-102 spectroreflectometer. The data were integrated with respect to the solar spectrum of air mass 0 to calculate the solar absorptance (α_s) values. Normal emittance (ϵ_T) was measured using a Gier-Dunkle DB-100 infrared reflector. In some cases, reflectance measurements were also made with a DK-2 spectrometer for comparison purposes.

Optical data for Z93 and YB-71 from these early studies are shown in Tables 24 and 25. Spectral curves generated with both the LPSR and the DK-2 are shown in Figures 7 through 20. The data for Z93 show the following:

1. The α_s for samples using the different silicate binders were in the 0.15 to 0.17 range when measured with the LPSR. Based on general earlier data in the literature, a range of about 0.14 to 0.17 may be expected.
2. The DK-2 values were somewhat higher than the LPSR data. The spectral curves show the IR portion to be slightly lower in reflectance.
3. The shapes of the curves in all of the samples were quite similar, indicating no significant effect from the substitution of Kasil 2130 or Kasil-1 for PS7 in Z93.

The results for YB-71 are tabulated in Table 25, and the reflectance curves are shown in Figures 15 through 20. The solar absorptance values for ZOT samples incorporating Kasil 2130 or Kasil-1 were somewhat higher than those for the PS7 samples. As was the case with the Z93 samples, DK-2 absorption values were slightly higher than the LPSR data, and the spectral responses at different wavelengths was similar for samples incorporating the different silicates.

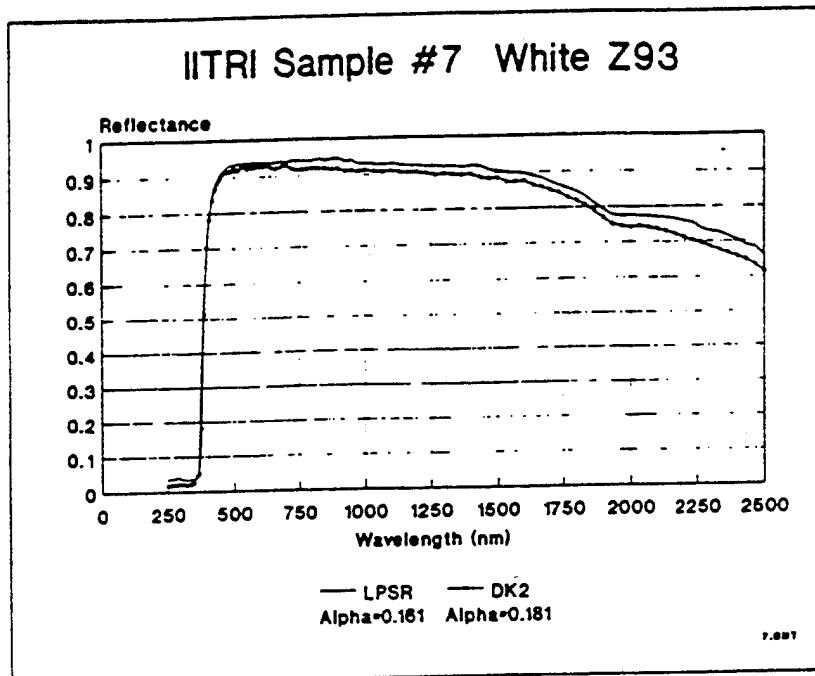


Figure 7. Reflectance of Sample 7: Z-93/PS-7 Original Formulation.
(Measured by AZ Technology)

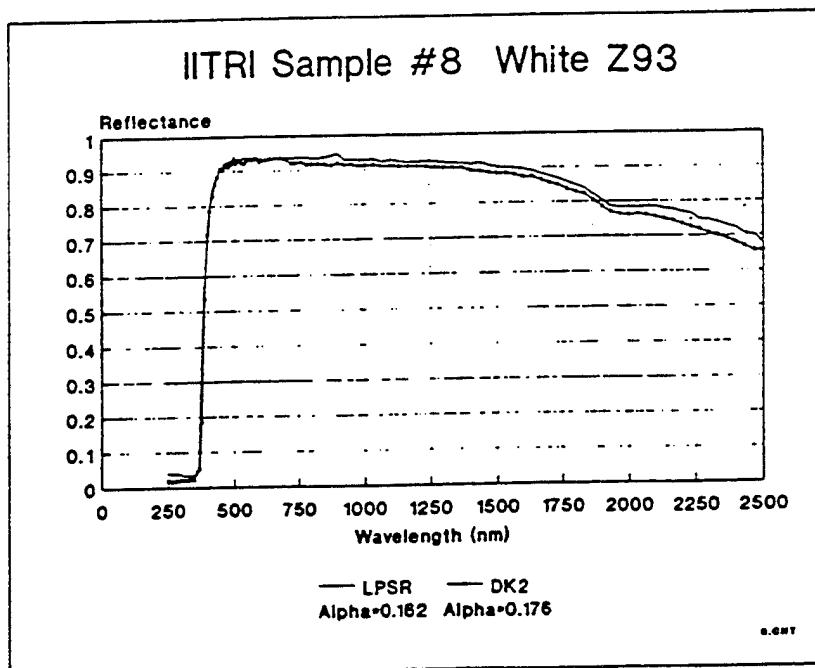


Figure 8. Reflectance of Sample 8: Z-93/PS-7 Original Formulation.
(Measured by AZ Technology)

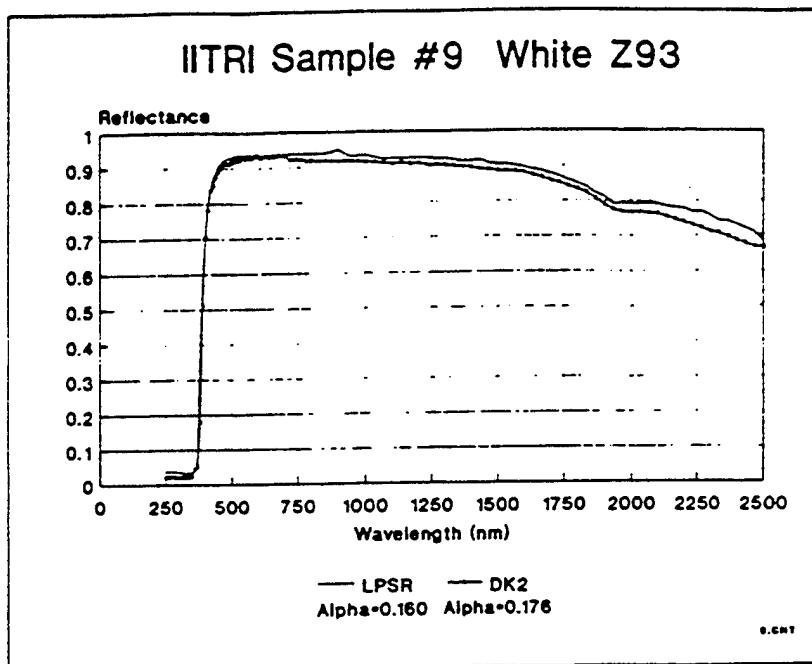


Figure 9. Reflectance of Sample 9: Z-93/PS-7 Original Formulation.
(Measured by AZ Technology)

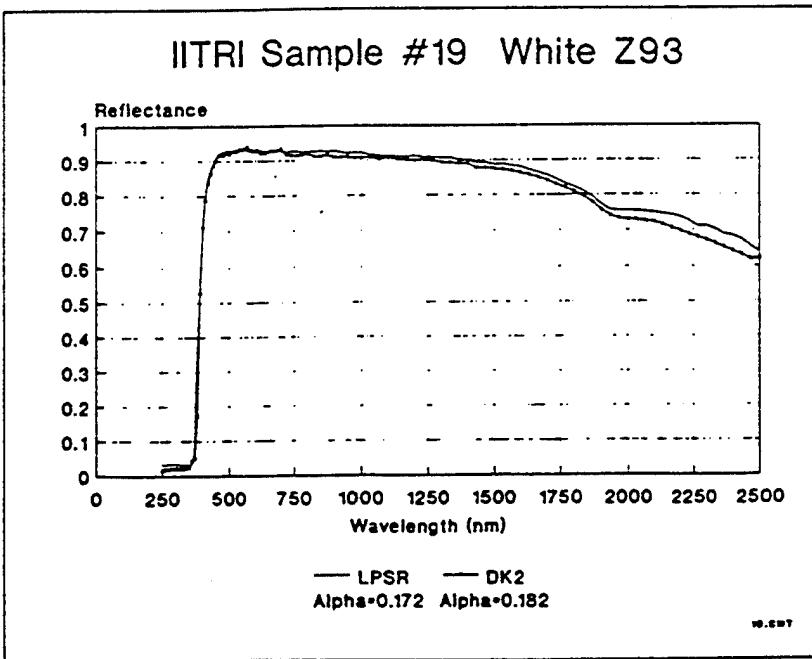


Figure 10. Reflectance of Sample 19: Z-93/2130.
(Measured by AZ Technology)

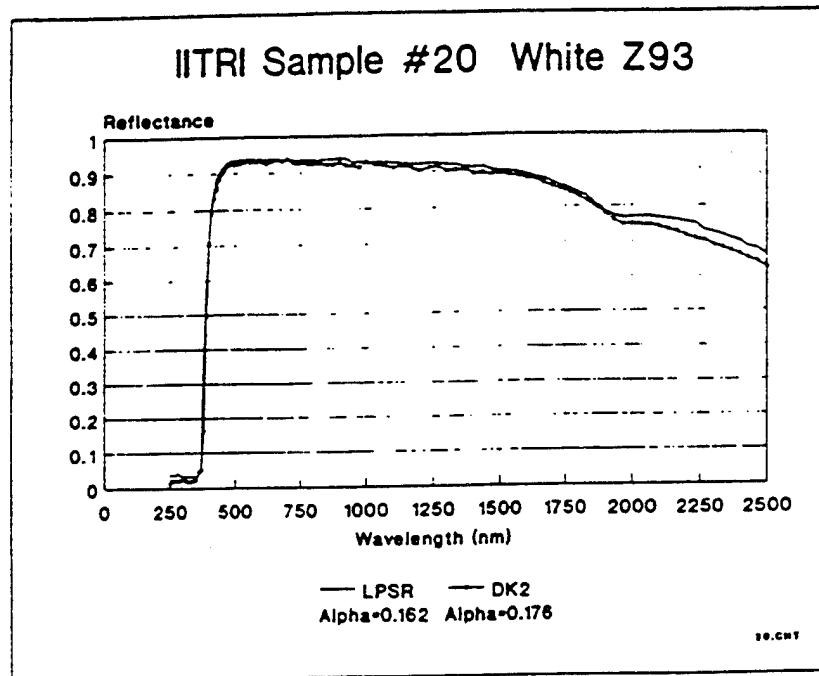


Figure 11. Reflectance of Sample 20: Z-93/2130.
(Measured by AZ Technology)

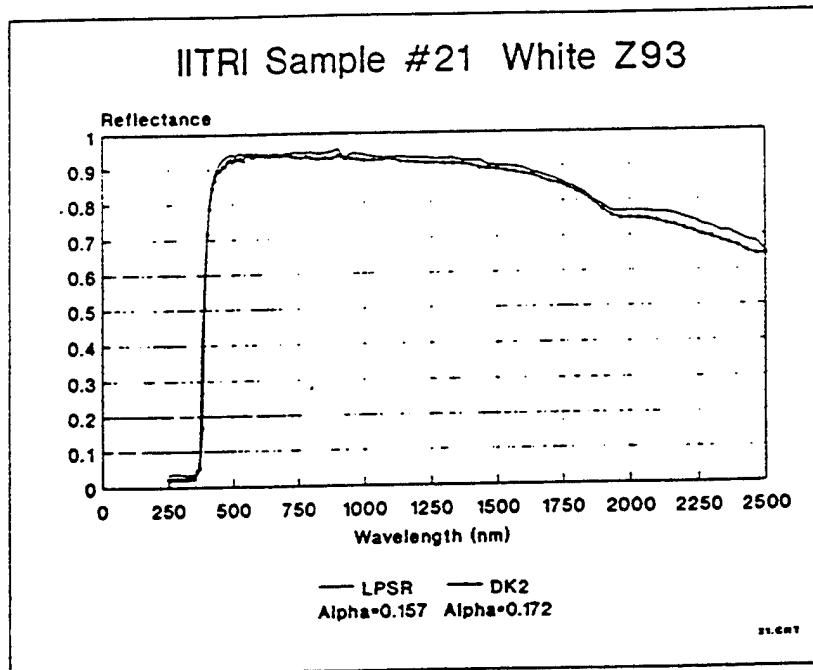


Figure 12. Reflectance of Sample 21: Z-93/2130.
(Measured by AZ Technology)

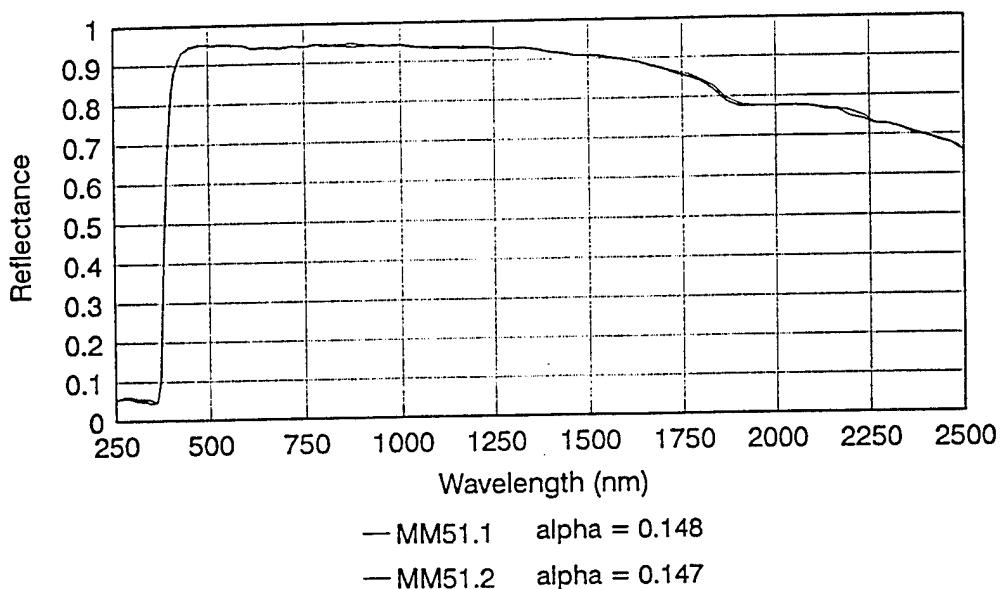


Figure 13. Reflectance Data for Sample MM51: Z-93/Kasil-1.

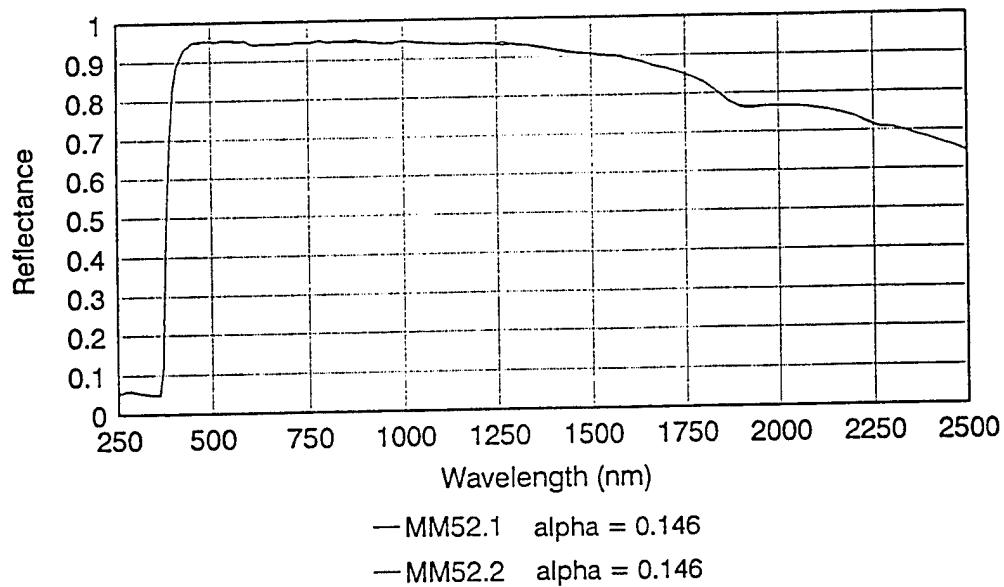


Figure 14. Reflectance Data for Sample MM52: Z-93/Kasil-1.

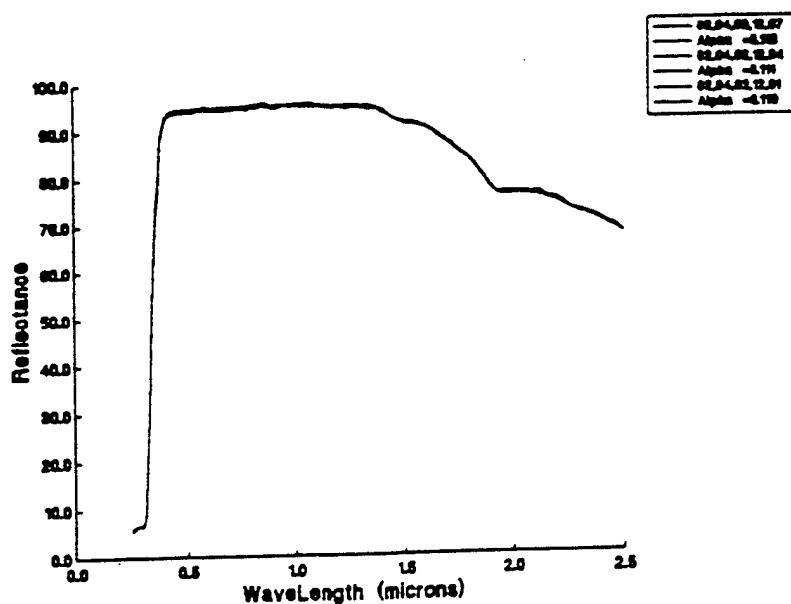


Figure 15. Reflectance of Samples 13, 14, 18: YB-71/PS-7 Original Formulation.
(Measured by AZ Technology)

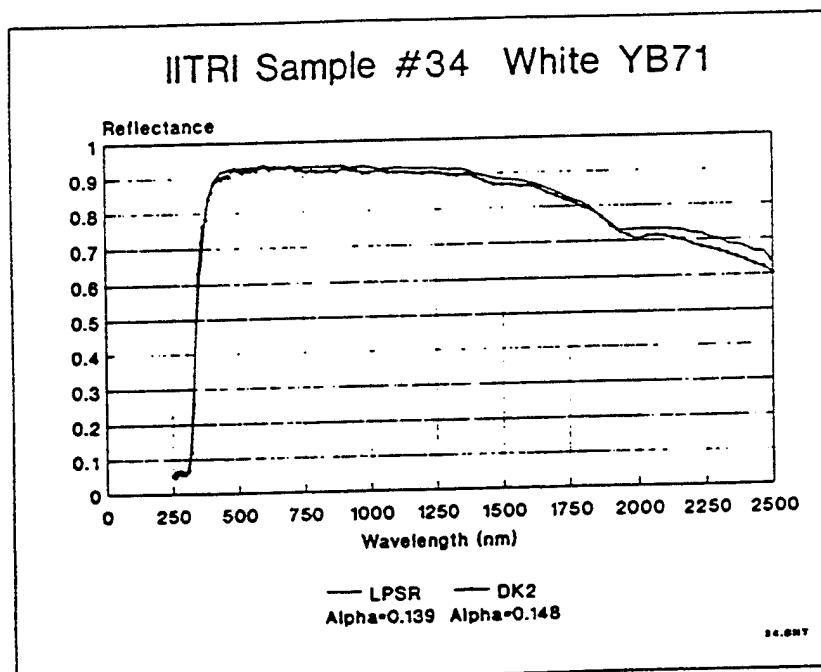


Figure 16. Reflectance of Sample 34: YB-71/2130.
(Measured by AZ Technology)

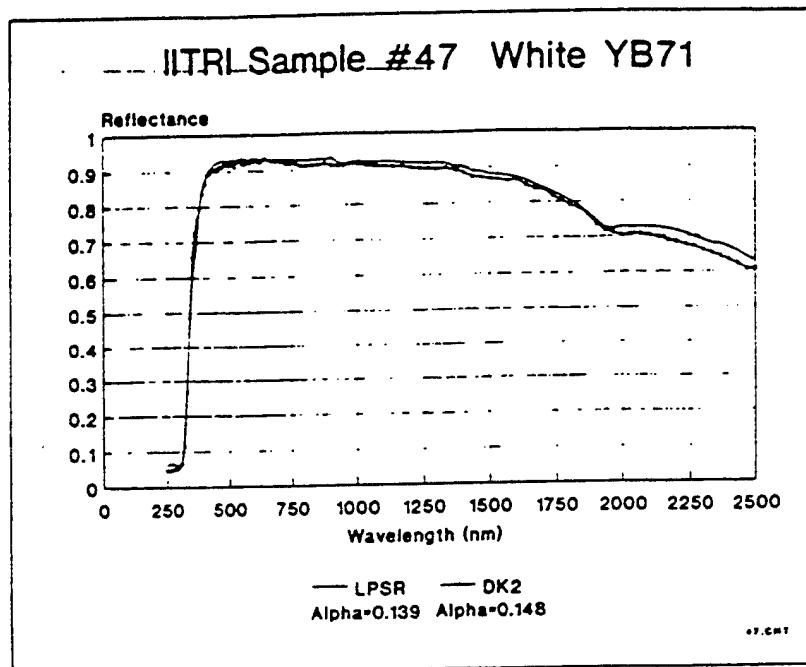


Figure 17. Reflectance of Sample 47: YB-71/2130.
(Measured by AZ Technology)

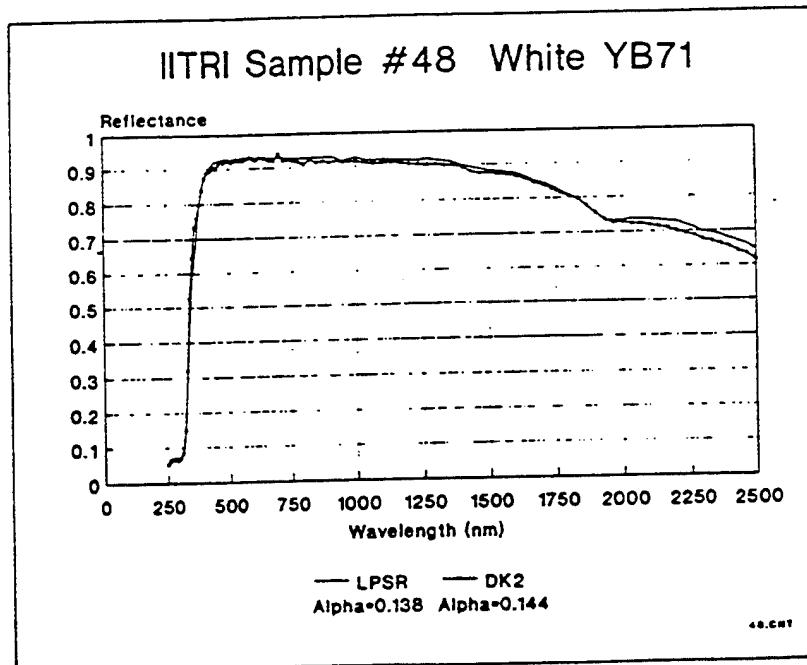


Figure 18. Reflectance of Sample 48: YB-71/2130.
(Measured by AZ Technology)

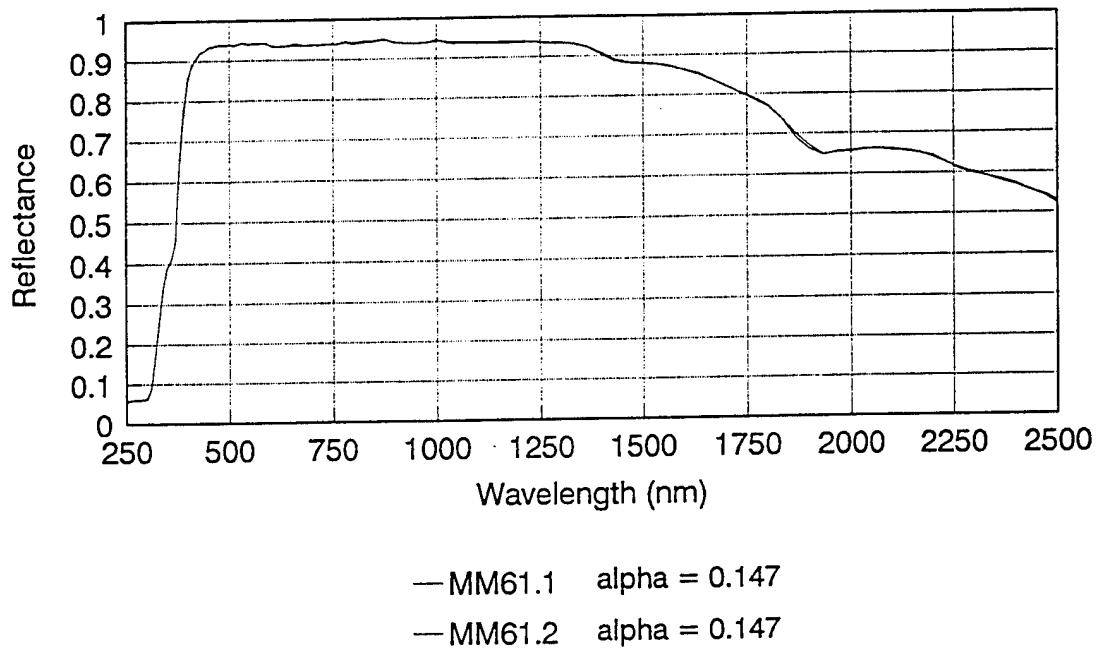


Figure 19. Reflectance Data: Sample MM61 (YB-71/Kasil-1).

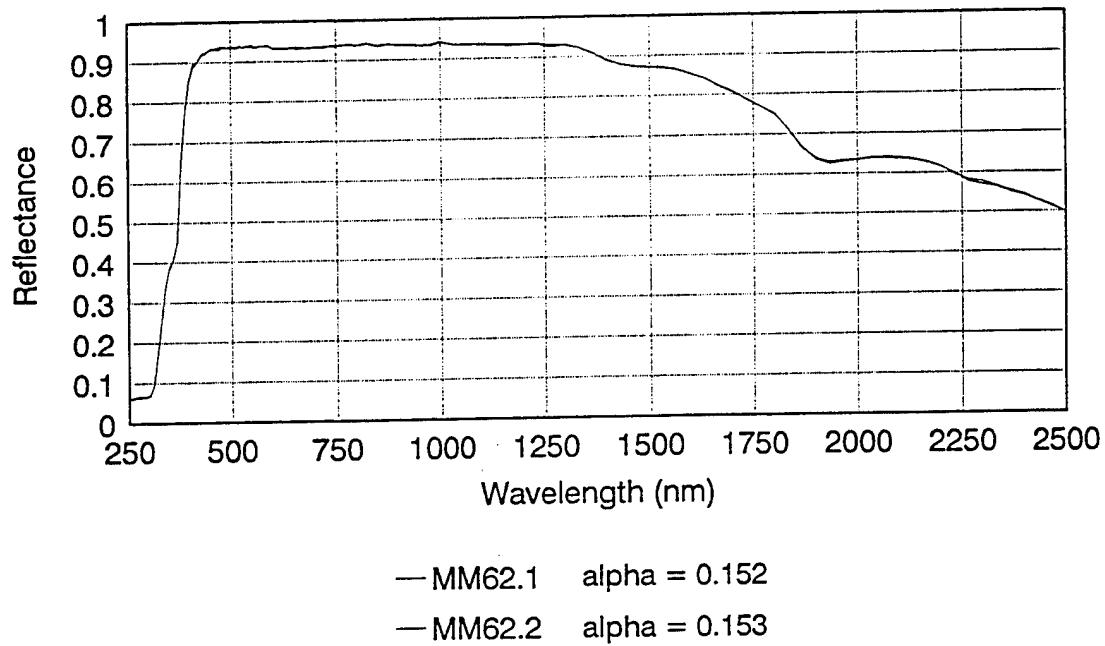


Figure 20. Reflectance Data: Sample MM62 (YB-71/Kasil-1).

TABLE 24. OPTICAL PROPERTIES OF Z-93 FORMULATIONS

Formulation & Sample No.	Batch No.	Coating Thickness, mils	Wt. of Coating, gms	Coating Density, gms/cc	Solar (α_s) Absorptance		Emittance (ϵ)
					LPSR	DK-2	
Z-93/PS-7 -7	R009	5.4	0.1061	1.54	.161	.181	0.914
Z-93/PS-7 -8		5.3	0.1059	1.57	.162	.176	0.915
Z-93/PS-7 -9		5.0	0.1071	1.68	.160	.176	0.919
Z-93/2130 -19	R016	5.7	0.1250	1.72	.172	.182	0.920
Z-93/2130 -20		5.9	0.1284	1.71	.162	.176	0.919
Z-93/2130 -21		6.1	0.1361	1.75	.157	.172	0.917
Z-93/Kasil-1 -51	R018	4.5	0.1168	2.00	.147		0.920
Z-93/Kasil-1 -52		5.1	0.1299	1.96	.146		0.920
Z-93 (typical)*		5.0 +2.0 -1.0			< 0.18		>0.80

*Typical requirements of reformulated Z-93, as described in Work Statement, Table 3 of Contract No. F33615-91-C-5554, p. 6, December 1990.

TABLE 25. OPTICAL PROPERTIES OF YB-71 FORMULATIONS

Formulation & Sample No.	Batch No.	Coating Thickness, mils	Wt. of Coating, gms	Coating Density, gms/cc	Solar (α_s) Absorptance		Emittance (ϵ)
					LSPR	DK-2	
YB-71/PS-7 -13		12.6	0.4707	2.93	0.1110		0.896
YB-71/PS-7 -14	R026	13.1	0.5021	3.01	0.1111		0.894
YB-71/PS-7 -18		13.0	0.4667	2.82	0.1118		0.892
YB-71/2130 -34		10.3	0.3796	2.89	0.139	0.148	0.877
YB-71/2130 -47	R028	10.1	0.3661	2.84	0.139	0.148	0.887
YB-71/2130 -48		9.8	0.3564	2.85	0.138	0.144	0.883
YB-71/Kasil-1 -61		10.7	0.4033	2.90	0.147		0.90
YB-71/Kasil-1 -62	R-053	9.8	0.3750	2.94	0.152		0.91
YB-71 (typical)*		8 to 14			< 0.15		> 0.80

*Typical requirements of reformulated YB-71:

YB-71 samples from Batches R-026 and R-028 have been evaluated on a Lambda-9 at the Aerospace Corporation (M. Meshishnek). The results shown in Table 26 indicate somewhat lower values for all samples, and the R-028 (Kasil 2130) specimens to be more reflective than the R-026 (PS7) in contrast to the AZ Technology data (Table 25). The lower absorptance values could be due to higher IR reflectance resulting from water removal in aging and/or difference in measurement techniques/equipment/test parameters.

**TABLE 26. YB-71 SAMPLE PRE-EXPOSURE SOLAR ABSORPTANCE
(Aerospace Corporation)**

Sample ID		Over Measurement Range
YBR026 (PS7)	#1	0.126
	#2	0.137
	#3	0.125
	#4	0.124
YBR028 (Kasil 2130)	#1	0.102
	#2	0.101
	#3	0.104
	#4	0.104
	#5	0.102
	#6	0.107

Reflectance measurements were also conducted at the Marshall Space Flight Center (Jason Vaughn) using the LPSR. The results of their measurement on samples from two other YB-71 batches are shown in Table 27, and spectral data are shown in Figure 21. A close similarity can be seen for the "old" and "new" YB-71 materials.

Data for S13 materials were also generated at NASA/MSFC by J. Vaughn. As shown in Table 27 and Figure 22, coatings involving PS7 or Kasil 2130 as the encapsulant for ZnO exhibited very similar optical behavior. S13GP/LO-1 from Batch R-055 (AZ Technology, LPSR) displayed somewhat higher reflectance spectra (Figures 23 and 24) with similar R vs. wavelength behavior.

**TABLE 27. OPTICAL PROPERTY DATA FOR IITRI COATINGS
(NASA/MSFC)**

Sample	Batch No.	Thickness (mils)	Solar Absorptance α	Emittance ϵ
S13G/LO-1 (PS7) X-29 X-30 X-31	S-174	7.9 7.3 8.0	0.203 0.209 0.210	0.917 0.917 0.918
S13GP/LO-1 (Kasil 2130) Y-29 Y-30 Y-31	S-174	7.8 7.4 7.9	0.204 0.203 0.202	0.908 0.909 0.903
YB-71 (PS7) C-002 C-011 C013	R-123	12.8 12.5 12.7	0.133 0.132 0.133	0.890 0.897 0.897
YB-71P (Kasil 2130) a 10 a 6 a 5	S-081	9.1 9.2 10.6	0.124 0.127 0.125	0.888 0.887 0.889

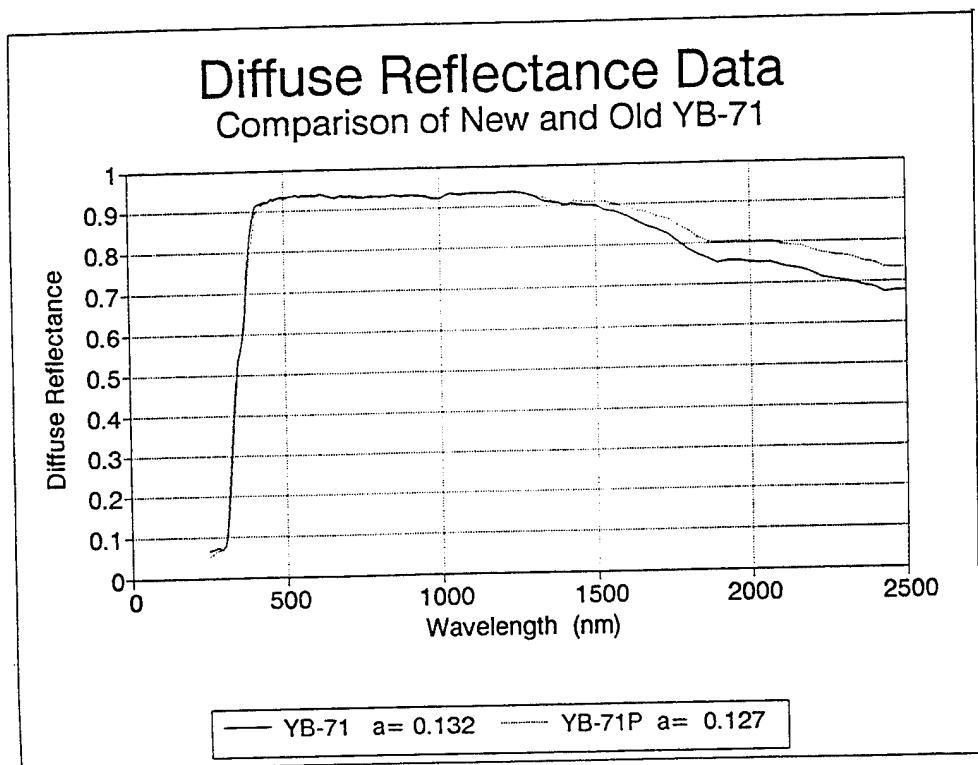


Figure 21. Diffuse Reflectance Data. Comparison of New and Old YB-71.

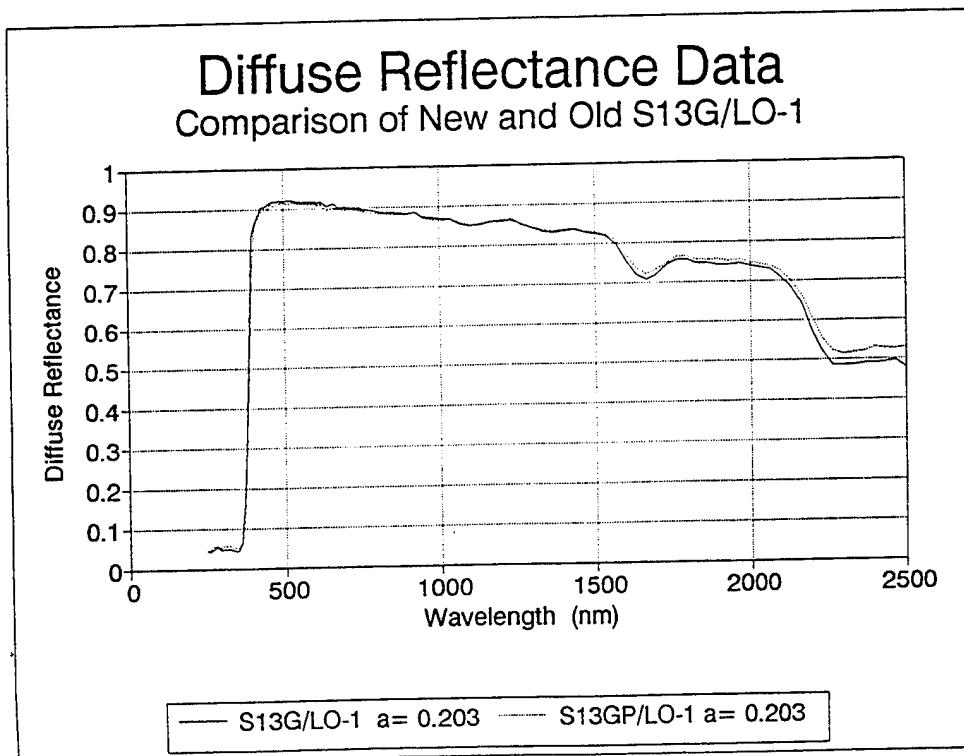


Figure 22. Diffuse Reflectance Data. Comparison of New and Old S13G/LO-1.

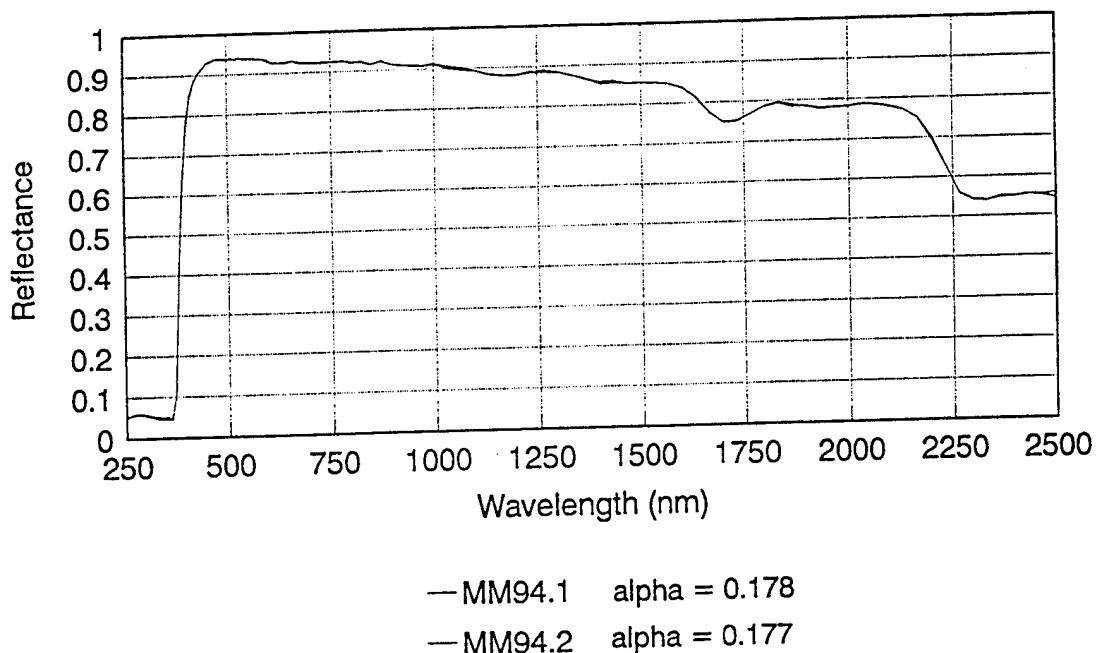


Figure 23. Reflectance Data for Sample MM94.
(S13G/LO-1, Kasil 2130, Batch R-055)

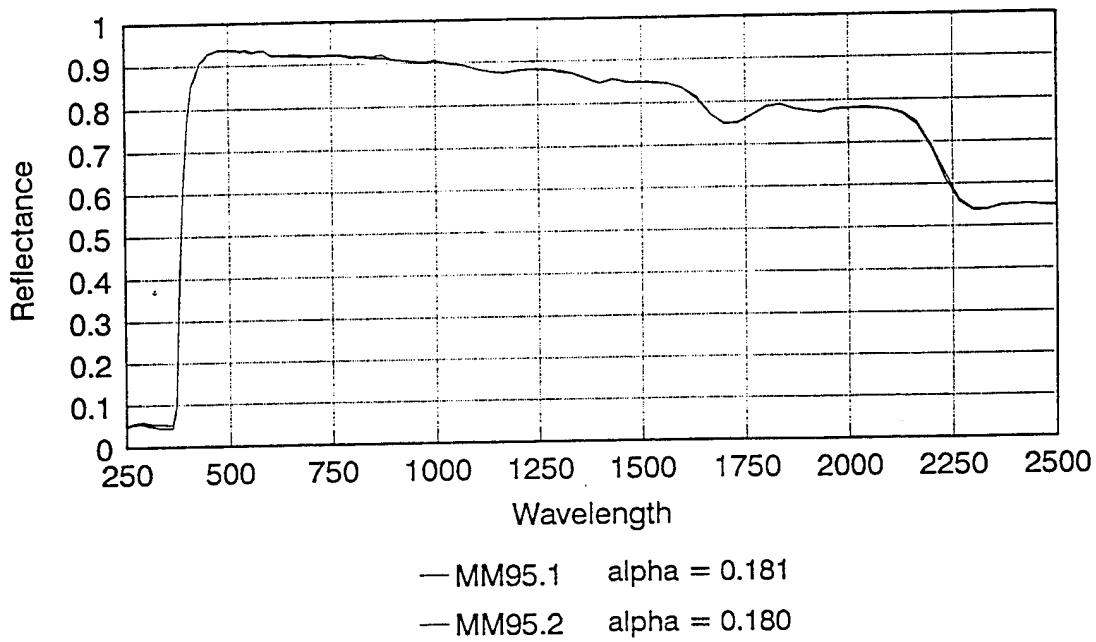


Figure 24. Reflectance Data for Sample MM95.
(S13G/LO-1, Kasil 2130, Batch R-055)

3.3.1.1 Coating Thickness Effects

The effect of coating thickness on optical properties were determined for Z93P and S13GP/LO-1. Data for solar absorptance and emittance vs thickness for Z93P are shown in Figures 25 and 26. These data indicate that maximum opacification is attained at a thickness of about 5 to 6 mils, and that maximum emittance is achieved at a thickness of about 2 to 3 mils. The thickness dependence data for S13GP/LO-1 presented in Figures 27 and 28 show a maximum opacification at about 8 mils and maximum emittance at about 5 mils. These results are similar to the behavior of earlier PS7 incorporating coatings.

In summary, the use of Kasil 2130 as a substitute for PS7 in Z93, S13G/LO-1 or YB-71 produced thermal control coating materials with optical properties quite similar to that for PS7 formulations.

3.3.2 Torsion Resistance

A torsion testing apparatus was designed to delineate differences in coating adhesion as a function of different parameters. The test assembly consists of the following:

- (1) 1/50 HP, 115 V, 1/180 worm gear reduction ratio, Bodine motor
- (2) 1:40 reduction ratio indexing chuck assembly
- (3) Coupling with zero backlash. (Threaded mounting for indexing spindle and spine mounting for Bodine's low rpm drive shaft.)
- (4) Fixed sample holder (fixed to the test fixture base plate)
- (5) Index marker to read angular position.

The assembled test apparatus is shown in Figure 29. The 1 inch x 3 inch sample is twisted through its longitudinal axis at a rate of 1° per second. The shear failure in torsion usually occurs with initial separation from the substrate at points A and B (see Figure 30).

Subsequent failure along the dotted line results almost immediately. The test is terminated at this point, and the angle-at-failure recorded. This test does not yield any absolute failure load stress values. However, it does serve to establish comparison of the adhesion behavior from sample to sample, and hence, reveal the effect of varying compositions, substrate materials, curing processes, etc.

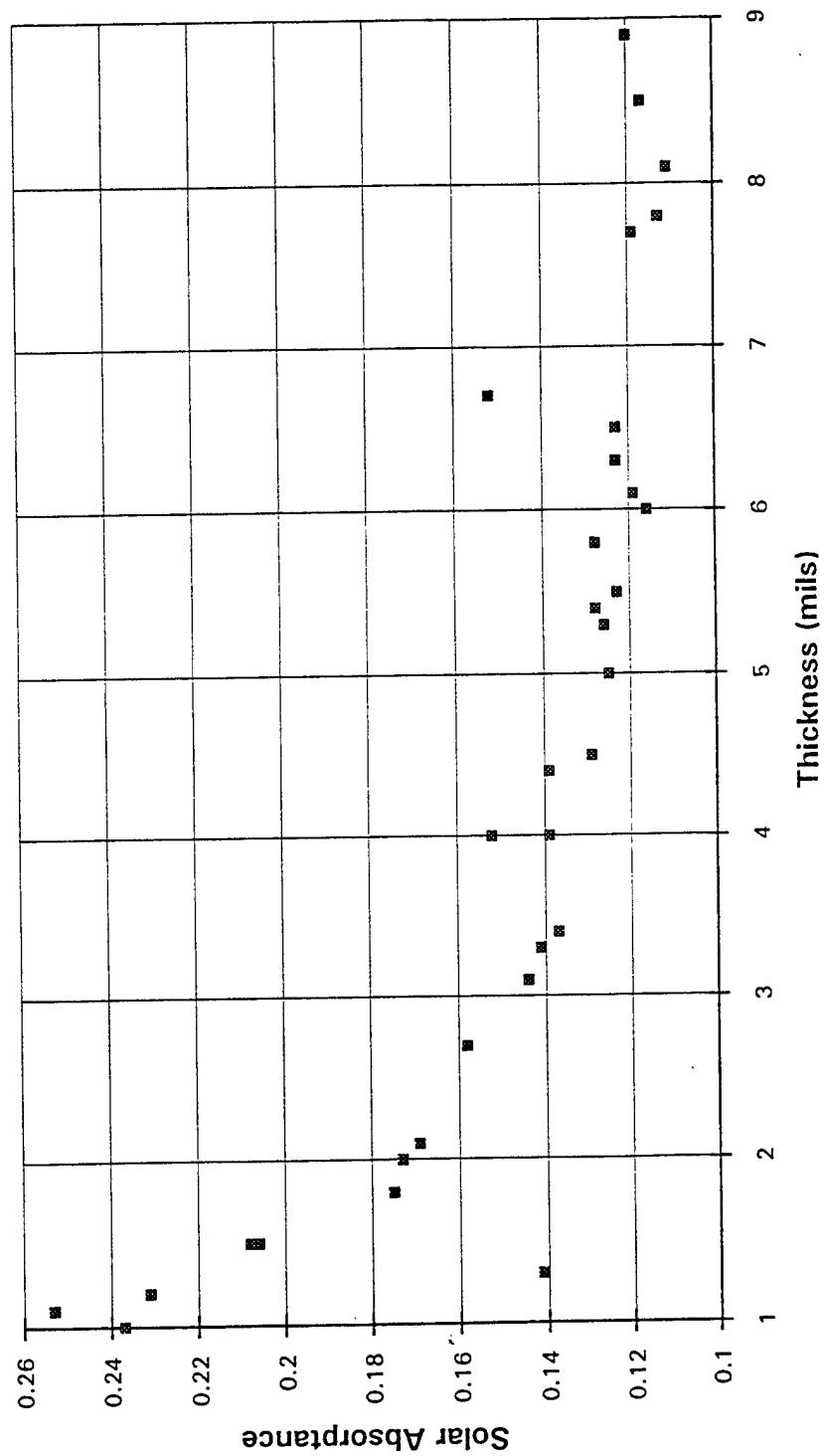


Figure 25. Solar Absorptance versus Thickness for Z-93P.

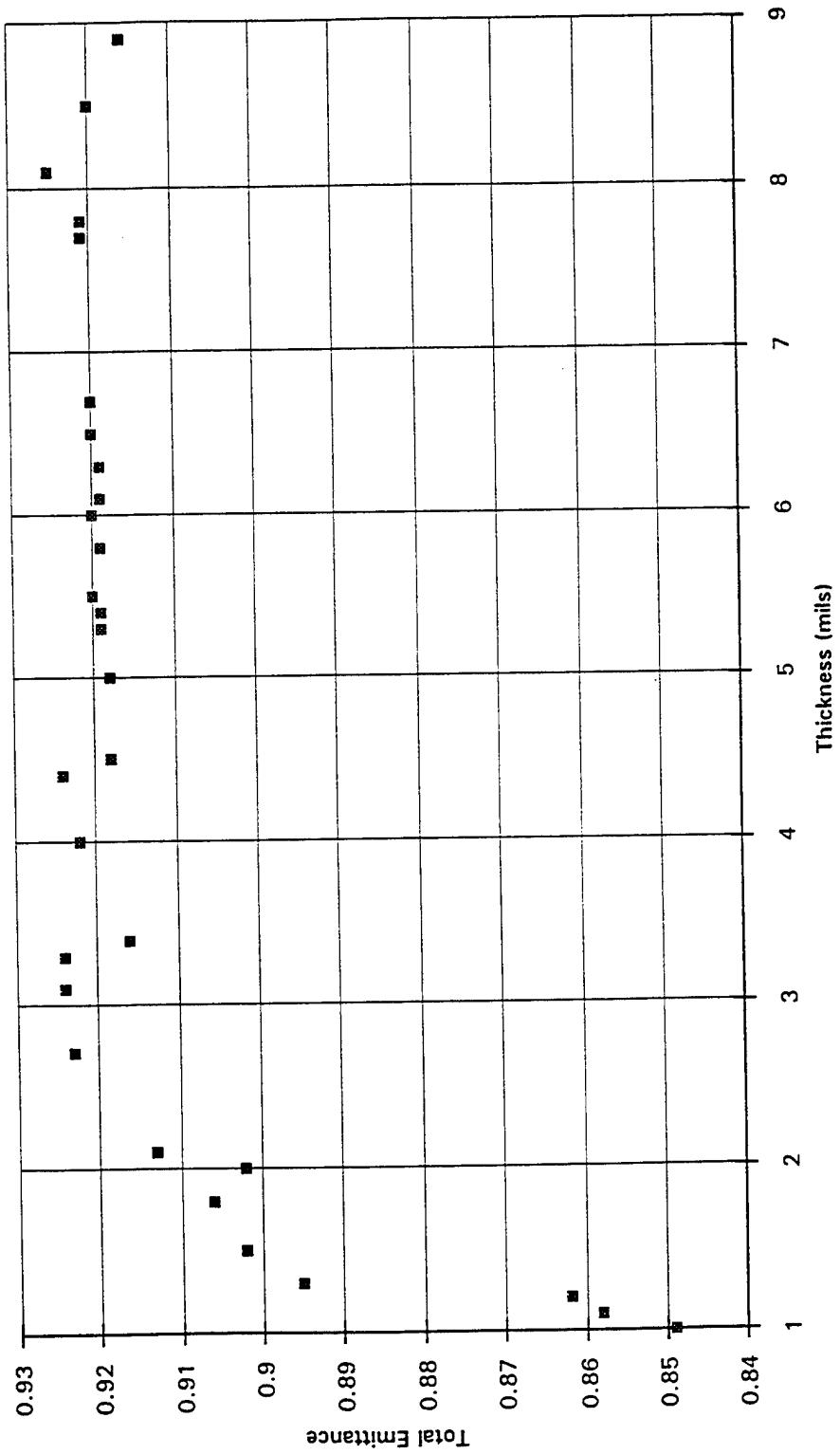


Figure 26. Total Emittance versus Thickness for Z-93P.

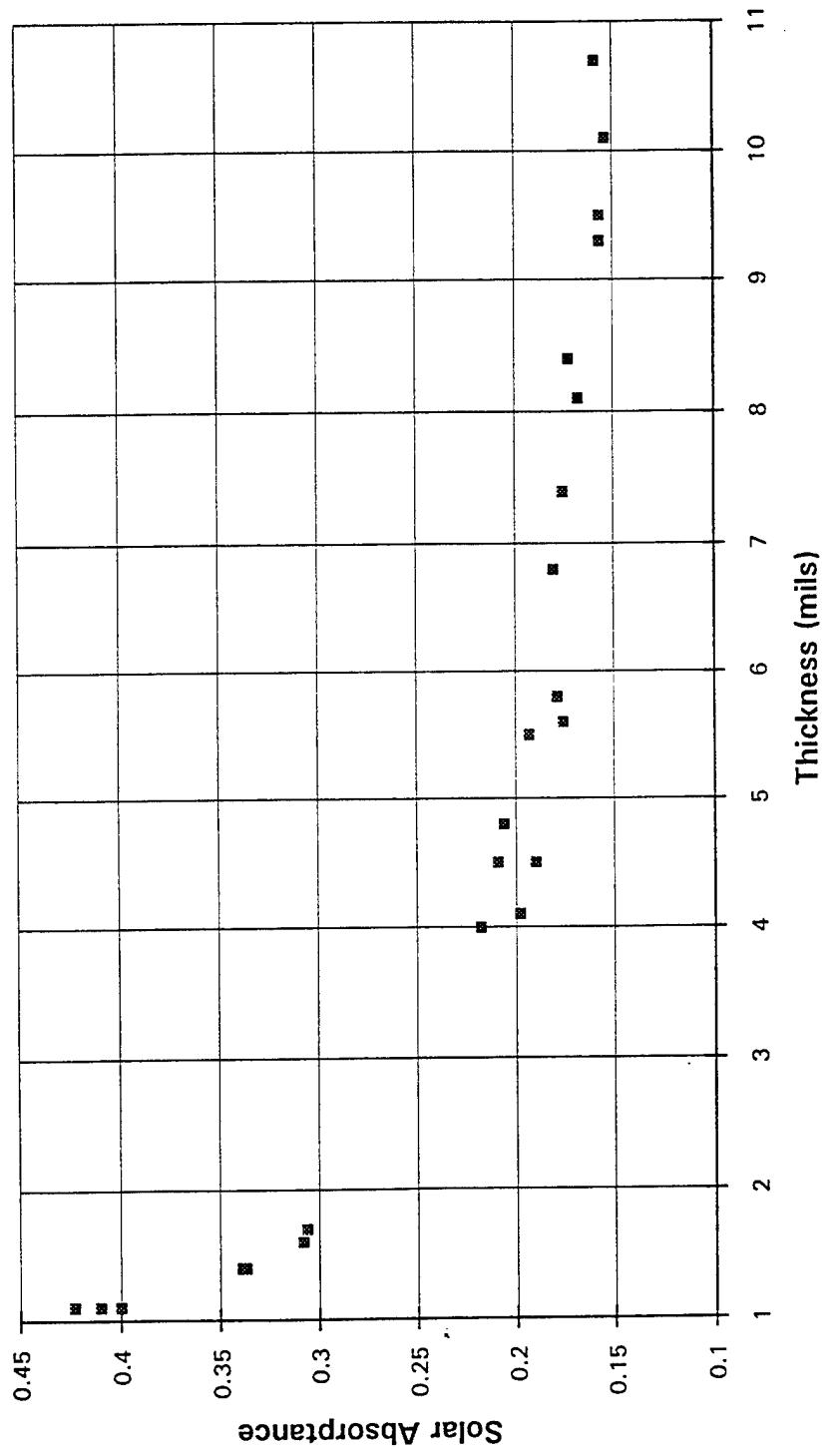


Figure 27. Solar Absorptance versus Thickness for S13GP/LO-1.

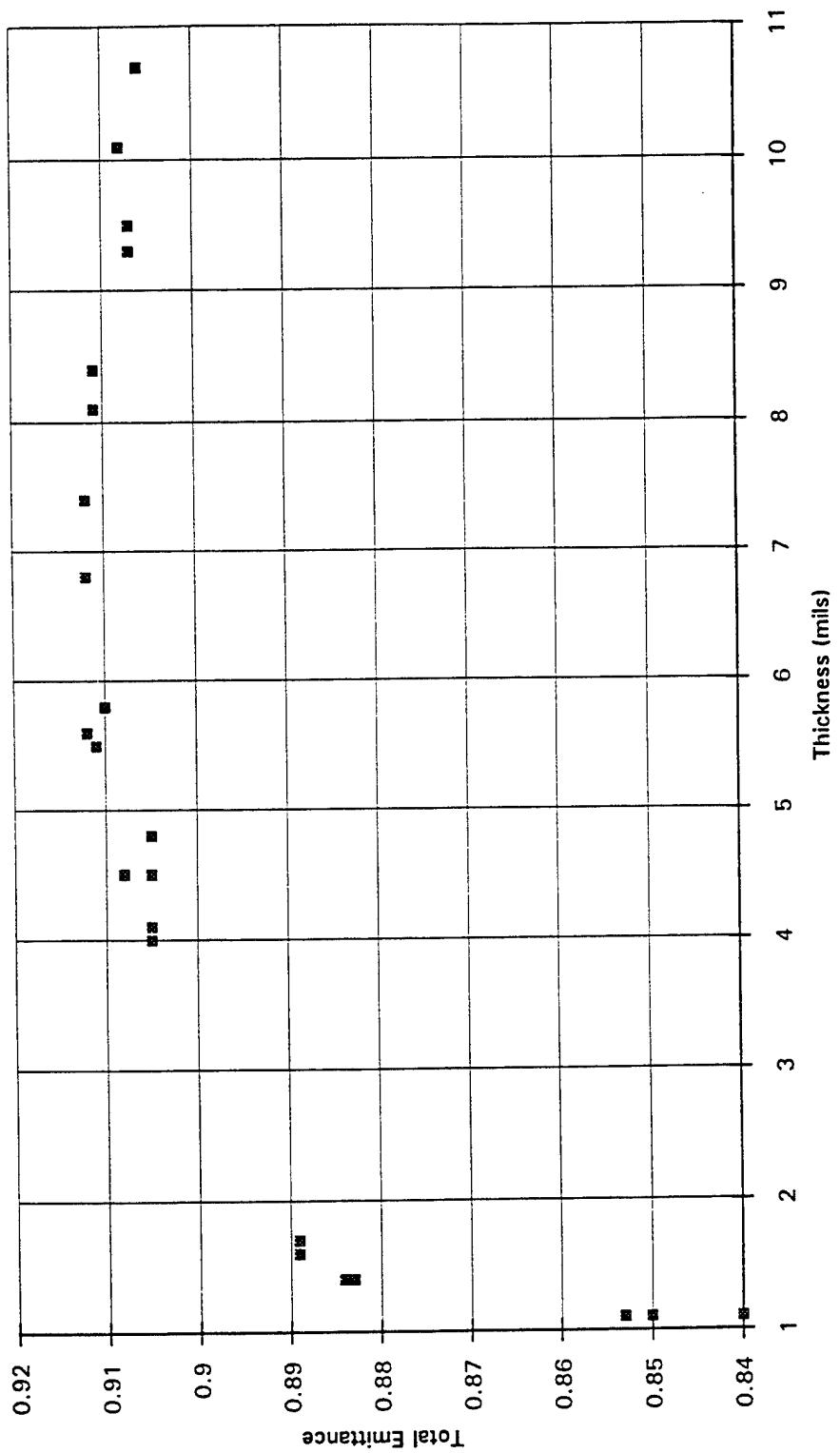


Figure 28. Total Emittance versus Thickness for S13GP/LO-1.

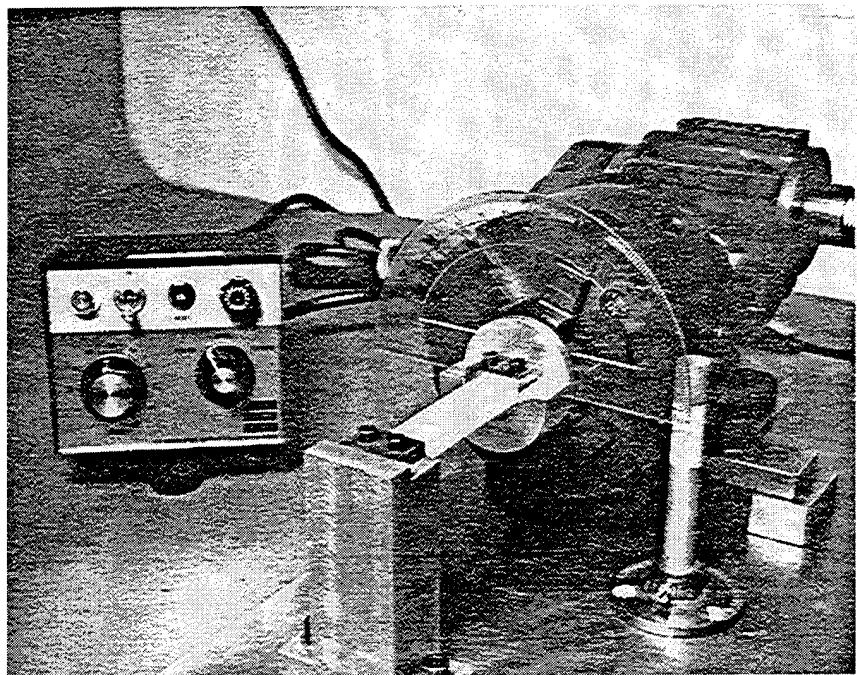


Figure 29. Torsion Test Apparatus.

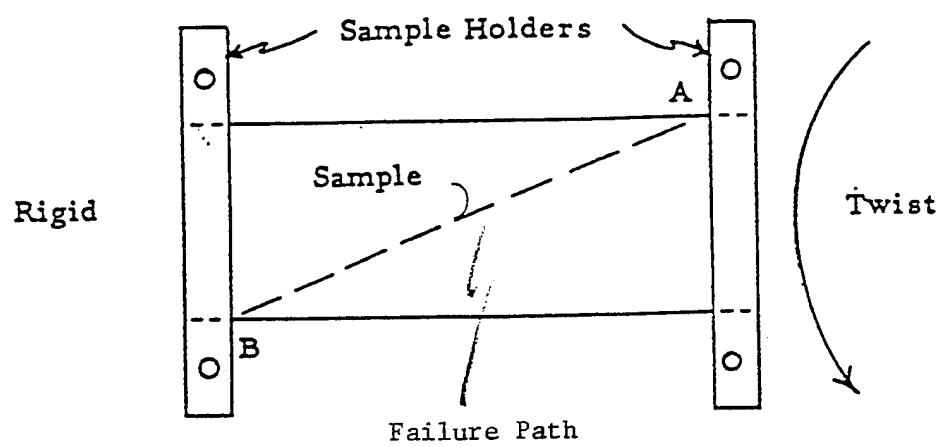


Figure 30. Schematic of Torsional Failure.

Substrates 1 inch x 3 inch (Al 6061) were mounted on spraying boards and sprayed with Z-93, YB-71 and candidate formulations Z-93P, Z-93K, YB-71P, and YB-71K. All were sprayed at the same time under the same temperature/humidity conditions, and cured under the same conditions. The results of the twist experiments are listed in Table 28 for Z-93 and Table 29 for YB-71. The values of twist angles at failure observed for Z-93 (PS7) sample are similar to those observed in the earlier studies² of 1963. Based on these results, the following conclusions can be drawn:

- (1) The twist torsion testing apparatus assembled for this program for 1 inch x 3 inch samples is capable of giving consistent results for twist angle at failure when a twisting rate of 1°/sec is used. The current Z-93 (PS7) results are consistent with the results of earlier studies for JPL.²
- (2) Kasil 2130 based Z-93P coatings exhibit adhesion behavior comparable or better than the Z-93 original formulation (with PS7), indicating that no variation in PBR (pigment-to-binder ratio) is needed.
- (3) Kasil-1 based Z-93K coatings show poorer adhesion performance than the Z-93 original formulation (with PS7). A variation in PBR is required for achieving improved adhesion performance.
- (4) The conclusion (2) also holds for the formulation YB-71P, which uses Kasil 2130 as the binder. YB-71P has comparable or better adhesion performance than YB-71.
- (5) The conclusion (3) also holds for the formulation YB-71K, which uses Kasil-1 as the binder. YB-71K is poorer in adhesion behavior than YB-71.

As an adjunct to this program, a study was conducted at IITRI for McDonnell Douglas Space Systems Company (MDA) comparing the torsional resistance of different Z93 formulations applied on different aluminum surfaces. A report on this study shows good adhesion for the Z93P incorporating Kasil 2130.

3.3.3 Thermal-Vacuum Testing - Humidity Resistance

Thermal-vacuum and humidity resistance testing were performed at NASA/MSFC by Miria Finkenour, EH41. Coating samples were prepared at IITRI on 6061-T6 substrates measuring 4 inches x 6 inches and submitted to MSFC. The data for these samples are shown in Table 30.

TABLE 28. RESULTS OF TORSION TEST FOR Z-93

Formulation	Sample No.	Thickness, mils	Twist Angle at Failure (Degrees, °)	Av. Twist Angle at Failure (Degrees, °)	Remarks
Z-93 (PS7)	0-1	6.4	65		
	0-2	6.3	68		
	0-3	5.9	75		
	0-4	6.4	69		
	0-5	7.2	65		
Z-93-P (Kasil 2130)	P-1	5.8	80		
	P-3	5.0	80		
	P-7	5.5	82		
	P-8	5.5	77		
Z-93-K (Kasil 1)	K1	7.0	49		
	K5	5.9	45		
	K7	6.5	45		
	K8	6.5	46		
				46.3	Interfacial adhesion bond for Z-93-P is somewhat stronger than the original Z-93 formulation.
					Interfacial adhesion bond for Z-93-K is weaker than the original Z-93.

**TABLE 29. RESULTS OF TORSION TEST FOR YB-71 AND CLONE
FORMULATIONS FOR YB-71-P AND YB-71-K**

Formulation	Sample No.	Thickness, mils	Twist Angle at Failure (Degrees, °)	Av. Twist Angle at Failure (Degrees, °)	Remarks
YB-71 (PS7)	Y1	8.03	72		
	Y4	8.43	69		
	Y6	7.72	68		
	Y8	7.00	75		
YB-71-P (Kasil 2130)	B5	8.35	65		
	B6	8.69	65		
	B7	8.95	64		
				64.7	Interfacial adhesion bond for YB-71-P is equal to that of original formulation.
YB-71-K (Kasil 1)	M5	9.63	45		
	M6	9.35	50		
	M7	9.01	44		
	M8	9.37	48	46.8	Interfacial adhesion bond for YB-71-K is somewhat weaker than that of original formulation.

TABLE 30. COATING SAMPLES FOR THERMAL-VACUUM TESTING
(Environmental Test Facility, NASA/MSFC)

Plate No.	Batch No.	Thickness, mils	Composition	Cycles	
				+65°C -95°C	+100°C -100°C
IITRI-1	S-044	3.8	Z-93-P	13,733	1559
IITRI-2	S-044	4.5	Z-93-P	-	1559
IITRI-3	S-044	4.5	Z-93-P	6853*	
IITRI-4	R-055	8.0	S13GP/LO-1		1559
IITRI-5	R-055	8.5	S13GP/LO-1	13,733	1559
IITRI-7	R-055	6.9	S13GP/LO-1	13,733	1559
IITRI-9	S-038	7.1	YB-Y1P		1559
IITRI-10	S-038	6.8	YB-71P	13,733	1559
IITRI-11	S-038	7.1	YB-71P	-	1559
IITRI-12	S-038	6.9	YB-71P	13,733	1559
IITRI-6	S-046	6.5	Z-93	13,733	1559
IITRI-8	S-046	7.0	Z-93	13,733	1559

$\sim 10^{-7}$ Torr

IR Quartz tube heaters and LN₂ Cooled Box

+65° -95°C/15 minutes

+100° C -100° C/60 minutes

* Run interrupted, loss of power. Slight cracking at corner, removed from chamber.

Thermal-vacuum cycling was conducted in the MSFC Environmental Test Facility. The vacuum level is maintained at 10^{-7} Torr, and two cycling series were used: $+65^{\circ}$ to -95°C in about 15 min for 13,733 cycles; and $+100^{\circ}$ to -100°C in about 1 hr for 1559 cycles. Thermal cycling rate is computer controlled using thermocouples attached to the backfaces of the specimen plates.

The initial run ($+65^{\circ}$ to -95°C) was interrupted after 6835 cycles due to a power loss. A Z-93P sample (IITRI-3), was removed at this point when a small crack on one corner was observed. However, it was not a gross failure. This run was continued to a total of 13,377 cycles, at the end of which no visual cracking or delamination was evident.

A second run using a different thermal cycle of $+100^{\circ}$ to -100°C was conducted on the samples which had already received the 13,733 ($+65^{\circ}$ to -95°C) cycles. Samples of Z-93P (IITRI-2), S13GP/LO-1 (IITRI-9), and YB-71P (IITRI-9 and -11) were added to the test chamber. No apparent spalling, cracking or delamination was observed on any sample after 1559 cycles. Photographs of selected samples are shown in Figures 31 through 34.

Humidity Resistance. Humidity resistance tests were conducted on some of the samples from the thermal-vacuum cycling tests. The test parameters were $40^{\circ}\text{C}/90 \pm 5\%$ R.H./48 hrs.

The two Z-93 paint samples, #6 and #8 failed adhesion testing after thermal cycling, so humidity testing was not performed on these samples. The samples received 13,733 thermal cycles between $+65$ and -90°C and 1559 thermal cycles of $\pm 100^{\circ}\text{C}$.

The Z-93P sample #1 also underwent 13,733 and 1559 thermal cycles. It performed satisfactorily during adhesion testing before and after humidity testing. The Z-93P sample #2 underwent only the 1559 thermal cycles $\pm 100^{\circ}\text{C}$. Some paint was pulled off during the second adhesion test but not enough to warrant failure of the sample.

The YB-71P sample #10 underwent 13,733 and 1559 thermal cycles. It performed satisfactorily during adhesion testing before and after humidity testing. Some fine cracking of the paint was noted at the bottom of the sample after humidity testing. The YB-71P sample #9 underwent 1559 thermal cycles $\pm 100^{\circ}\text{C}$. It performed satisfactorily during adhesion testing before and after humidity testing. Again, some fine cracking of the paint was noted at the bottom of the sample after humidity testing. Additional paint has flaked off at the adhesion test

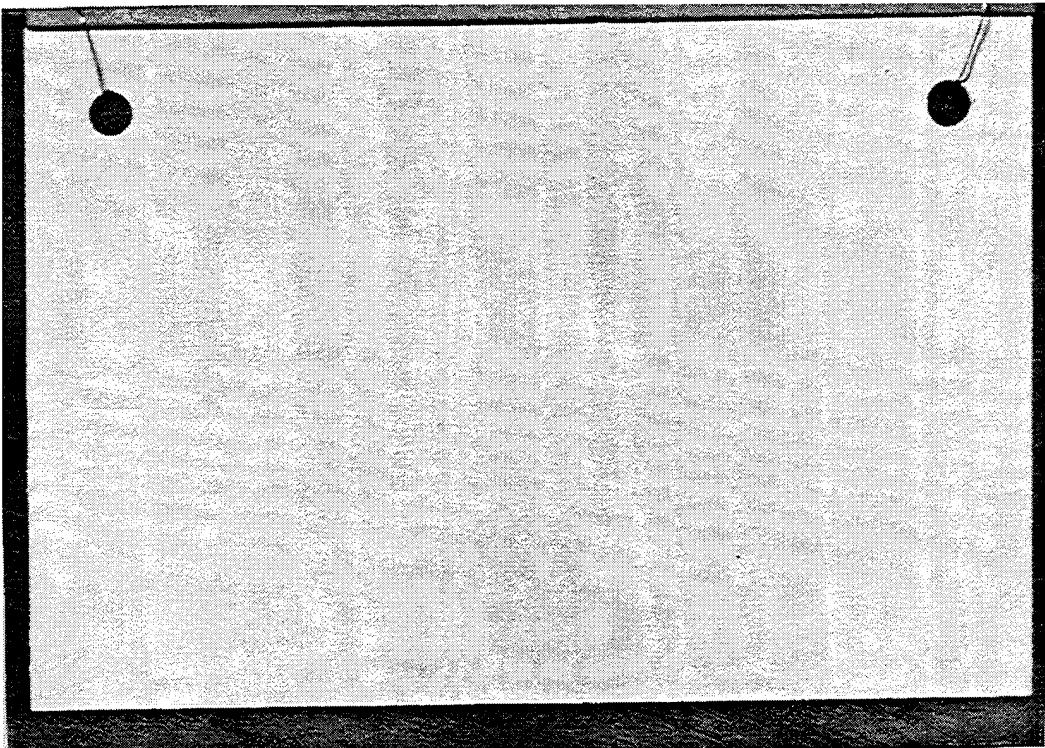


Figure 31. Photograph of Sample IITRI-8 (Z93)
After 13,733 Cycles of +65° to -95°C.

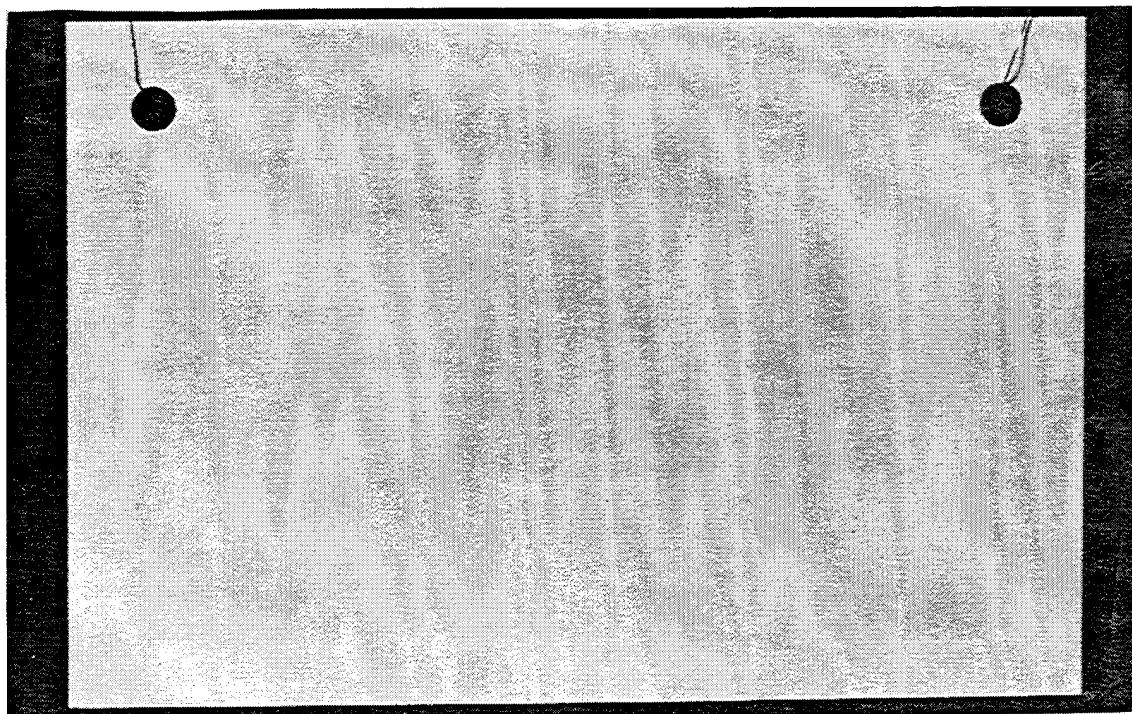


Figure 32. Photograph of Sample IITRI-10 (YB-71P)
After 13,733 Cycles of +65° to -95°C.

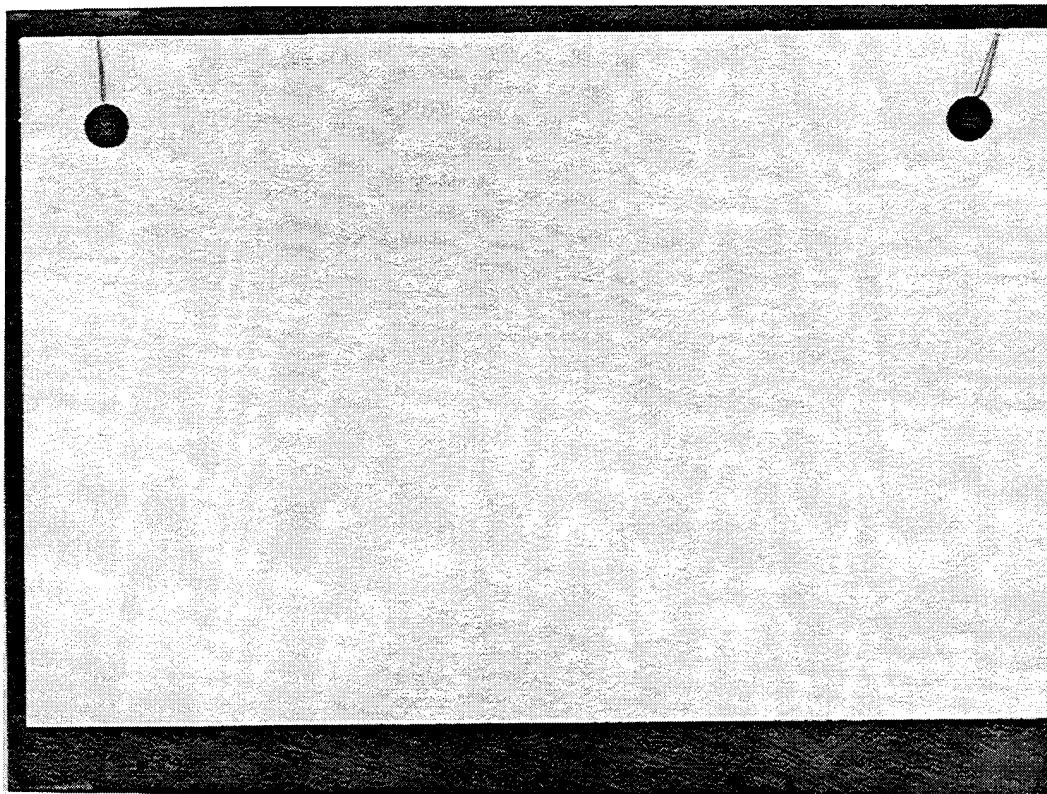


Figure 33. Photograph of Sample IITRI-5 (S13GP/LO-1)
After 13,733 Cycles of +65° to -95°C.

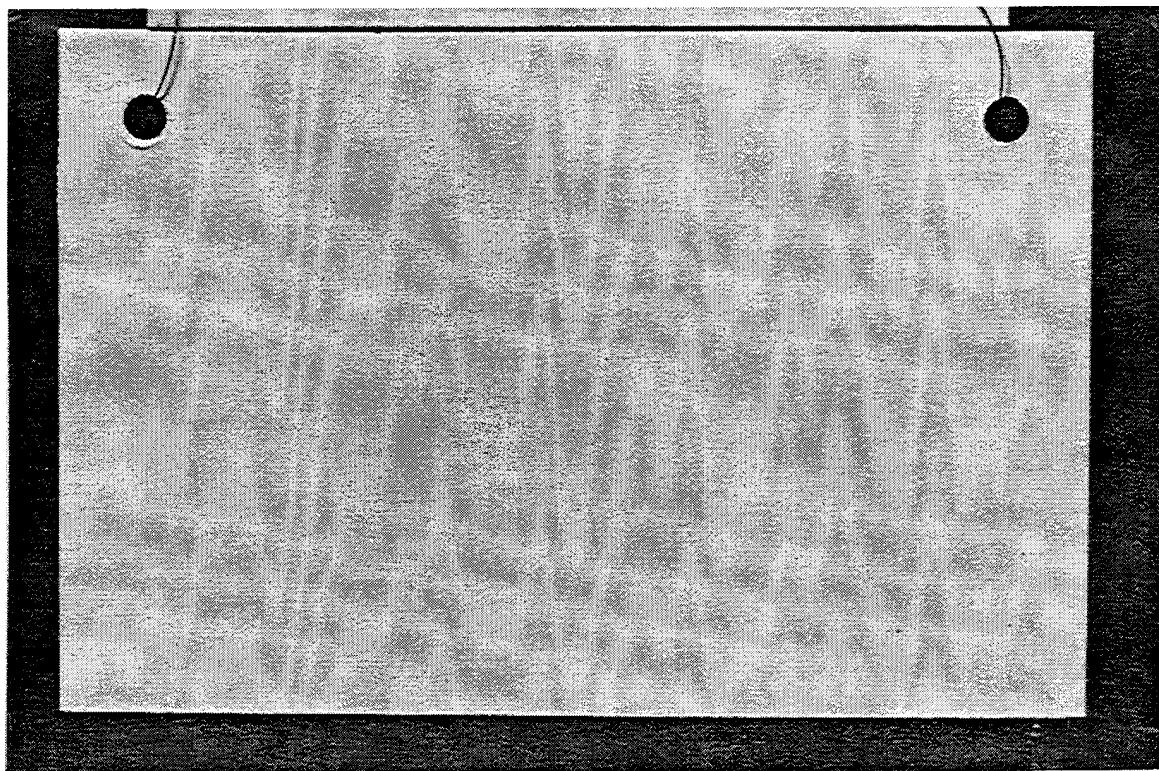


Figure 34. Photograph of Sample IITRI-1 (Z93P)
After 13,733 Cycles of +65° to -95°C.

site either due to the testing or handling. This was not noted at the time of test. Hence, it was believed that the flaking has occurred after the test was completed. Enough paint has flaked off to warrant failure of the sample. A third adhesion test performed just prior to shipment of the samples did not produce a failure.

The S13GP/LO-1 sample #5 underwent 13,733 and 1559 thermal cycles. It performed satisfactorily during adhesion testing before and after humidity testing. The S13GP/LO-1 sample #4 underwent 1559 thermal cycles $\pm 100^{\circ}\text{C}$. It performed satisfactorily during adhesion testing before and after humidity testing.

In summary, samples incorporating Kasil 2130 as the binder material (Z-93P and YB-71P) or as an encapsulant for ZnO (S13GP/LO-1) show satisfactory resistance to thermal-vacuum cycling and to a high humidity environment.

3.3.4 Outgassing Properties

Prepared batches of S13GP/LO-1 (R-055, S-168) were compared with typical batches of S13G/LO-1 (S-025, T-114) in outgassing tests. Cured samples of these batches were submitted to NuSil Technology Corporation for Total Mass Loss (TML) and Collectable Volatile Condensable Material (CVCM) tests following ASTM-E-595 and NASA-SP-R-0022A. The test reports shown in Tables 31a to 31g show that S13GP/LO-1, like S13G/LO-1, meets the TML/CVCM requirements for space application.

Z93 and YB-71 are water-based formulations which do not incorporate organic volatiles. Therefore, these materials were not submitted for this testing.

3.4 ENVIRONMENTAL TESTING

The important consideration for any requalified thermal control materials is that they exhibit stability to the space environment similar to that shown by the old formulations which incorporated PS7 potassium silicate. Space simulation testing of these materials have been, and are being conducted at different facilities. The following is a summary of these efforts. More detailed discussions will be prepared by the different agencies involved.

TABLE 31a. TEST REPORT FOR MASS LOSS AND COLLECTED VOLATILE CONDENSABLE MATERIALS (NuSil Silicone Technology)



NuSil Technology
1150 Mark Avenue
Carpinteria, CA 93013
FAX 805/566-0270
805/566-0275

TEST REPORT FOR MASS LOSS AND
COLLECTED VOLATILE CONDENSABLE MATERIALS
TESTING DONE IN ACCORDANCE WITH :

ASTM E-595
NASA SP-R-0022A
ESA PSS-01-702

SAMPLE NUMBER : 3496 TEST POSITION NUMBER : 1 P.O.#: 11-18915

CUSTOMER : IIT RESEARCH INSTITUTE
3441 SOUTH FEDERAL
CHICAGO, IL 60616
ATTENTION: Y. HARADA

MATERIAL TESTED: S13GP/LO-1 R-055 SAMPLE #1 LOT: N/A
TEST DATE: 12/29/93 TEST NUMBER: 1304 PRESSURE (torr): 2.0 E-7

RESULTS:
Total Mass Loss (TML): 0.42
Collected Volatile Condensable Material (CVCM): 0.00
Water Vapor Recovered (WVR): 0.25

OBSERVATIONS:
Visible Condensate: NO Transparent: N/A
Percent covered: N/A Opaque: N/A
Thin: N/A Interference fringes: N/A
Heavy: N/A Color of fringes: N/A

COMMENTS: N/A
N/A

Specimen appearance after test: NO CHANGE.

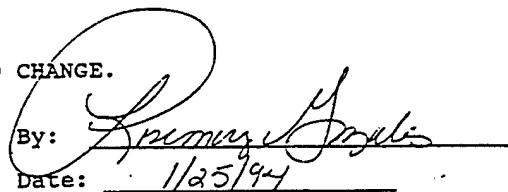
By: 
Date: 1/25/94

TABLE 31b. TEST REPORT FOR MASS LOSS AND COLLECTED VOLATILE CONDENSABLE MATERIALS (NuSil Silicone Technology)



NuSil Technology
1150 Mark Avenue
Carpinteria, CA 93013
FAX 805/566-0270
805/566-0275

TEST REPORT FOR MASS LOSS AND
COLLECTED VOLATILE CONDENSABLE MATERIALS
TESTING DONE IN ACCORDANCE WITH :

ASTM E-595
NASA SP-R-0022A
ESA PSS-01-702

SAMPLE NUMBER : 3497 TEST POSITION NUMBER : 2 P.O.#: 11-18915

CUSTOMER : IIT RESEARCH INSTITUTE
3441 SOUTH FEDERAL
CHICAGO, IL 60616
ATTENTION: Y. HARADA

ATTENTION: Y. HARADA

RESULTS: Total Mass Loss (TML): 0.33
 Collected Volatile Condensable Material (CVCM): 0.00
 Water Vapor Recovered (WVR): 0.17

OBSERVATIONS:

Visible Condensate:	NO	Transparent:	N/A
Percent covered:	N/A	Opaque:	N/A
Thin:	N/A	Interference fringes:	N/A
Heavy:	N/A	Color of fringes:	N/A

COMMENTS: N/A
N/A

Specimen appearance after test: NO CHANGE

CHANGE.

By: Brumley Dreyfus

Date: 1/25/94

TABLE 31c. TEST REPORT FOR MASS LOSS AND COLLECTED VOLATILE CONDENSABLE MATERIALS (NuSil Silicone Technology)



SILICONE
TECHNOLOGY

NuSil Technology
1150 Mark Avenue
Carpinteria, CA 93013
FAX 805/566-0270
805/566-0275

TEST REPORT FOR MASS LOSS AND
COLLECTED VOLATILE CONDENSABLE MATERIALS
TESTING DONE IN ACCORDANCE WITH :

ASTM E-595
NASA SP-R-0022A
ESA PSS-01-702

SAMPLE NUMBER : 3488 TEST POSITION NUMBER : 2 P.O.#: 11-18915

CUSTOMER : IIT RESEARCH INSTITUTE
3441 S. FEDERAL
CHICAGO, IL 60616
ATTENTION: Y. HARADA

MATERIAL TESTED: S13GP/LO-1 S-168 SAMPLE #1 LOT: N/A
TEST DATE: 12/23/93 TEST NUMBER: 1302 PRESSURE (torr): 1.5 E-6

RESULTS:
Total Mass Loss (TML): 0.63
Collected Volatile Condensable Material (CVCM): 0.02
Water Vapor Recovered (WVR): 0.53

OBSERVATIONS:
Visible Condensate: YES Transparent: YES
Percent covered: 50-60% Opaque: NO
Thin: YES Interference fringes: NO
Heavy: NO Color of fringes: N/A

COMMENTS: CONDENSATE WHITE IN APPEARANCE.
N/A

Specimen appearance after test: NO CHANGE.

By: Ronny Angels
Date: 12/28/93

**TABLE 31d. TEST REPORT FOR MASS LOSS AND COLLECTED VOLATILE
CONDENSABLE MATERIALS (NuSil Silicone Technology)**



NuSil Technology
1150 Mark Avenue
Carpinteria, CA 93013
FAX 805/566-0270
805/566-0275

TEST REPORT FOR MASS LOSS AND
COLLECTED VOLATILE CONDENSABLE MATERIALS
TESTING DONE IN ACCORDANCE WITH :

ASTM E-595
NASA SP-R-0022A
ESA PSS-01-702

SAMPLE NUMBER : 3489 TEST POSITION NUMBER : 3 P.O.#: 11-18915

CUSTOMER : IIT RESEARCH INSTITUTE
3441 S. FEDERAL
CHICAGO, IL 60616
ATTENTION: Y. HARADA

MATERIAL TESTED: S13GP/LO-1 S-168 SAMPLE #2 LOT: N/A
TEST DATE: 12/23/93 TEST NUMBER: 1302 PRESSURE (torr): 1.5 E-6

RESULTS:
Total Mass Loss (TML): 0.58
Collected Volatile Condensable Material (CVCM): 0.02
Water Vapor Recovered (WVR): 0.65

OBSERVATIONS:
Visible Condensate: YES Transparent: YES
Percent covered: 50-60% Opaque: NO
Thin: YES Interference fringes: NO
Heavy: NO Color of fringes: N/A

COMMENTS: CONDENSATE WHITE IN APPEARANCE.
N/A

Specimen appearance after test: NO CHANGE.

By: Rosemary Gonzales
Date: 1/25/94

TABLE 31e. TEST REPORT FOR MASS LOSS AND COLLECTED VOLATILE CONDENSABLE MATERIALS (NuSil Silicone Technology)



NuSil Technology
1150 Mark Avenue
Carpinteria, CA 93013
FAX 805/566-0270
805/566-0275

TEST REPORT FOR MASS LOSS AND
COLLECTED VOLATILE CONDENSABLE MATERIALS
TESTING DONE IN ACCORDANCE WITH :

ASTM E-595
NASA SP-R-0022A
ESA PSS-01-702

SAMPLE NUMBER : 3513 TEST POSITION NUMBER : 5 P.O.#: 11-18915

CUSTOMER : IIT RESEARCH INSTITUTE
3441 SOUTH FEDERAL
CHICAGO, IL 60616
ATTENTION: Y. HARADA

MATERIAL TESTED: S13G/LO-1, S-025 SAMPLE #1 LOT: N/A
TEST DATE: 01/12/94 TEST NUMBER: 1307 PRESSURE (torr): 2.0 E-6

RESULTS:
Total Mass Loss (TML): 0.51
Collected Volatile Condensable Material (CVCM): 0.02
Water Vapor Recovered (WVR): 0.08

OBSERVATIONS:
Visible Condensate: YES Transparent: YES
Percent covered: 50-60% Opaque: NO
Thin: YES Interference fringes: NO
Heavy: NO Color of fringes: N/A

COMMENTS: CONDENSATE WAS LIGHT
BLUE IN APPEARANCE.

Specimen appearance after test: NO CHANGE.

By: Rosemary Gonzalez
Date: 1/25/94

**TABLE 31f. TEST REPORT FOR MASS LOSS AND COLLECTED VOLATILE
CONDENSABLE MATERIALS (NuSil Silicone Technology)**



SILICONE
TECHNOLOGY

NuSil Technology
1150 Mark Avenue
Carpinteria, CA 93013
FAX 805/566-0270
805/566-0275

TEST REPORT FOR MASS LOSS AND
COLLECTED VOLATILE CONDENSABLE MATERIALS
TESTING DONE IN ACCORDANCE WITH :

ASTM E-595
NASA SP-R-0022A
ESA PSS-01-702

SAMPLE NUMBER : 3517 TEST POSITION NUMBER : 3 P.O.#: 11-18915

CUSTOMER : IIT RESEARCH INSTITUTE
3441 SOUTH FEDERAL
CHICAGO, IL 60616
ATTENTION: Y. HARADA

MATERIAL TESTED: S13G/LO-1, S-025 SAMPLE #2

LOT: N/A

TEST DATE: 01/14/94 TEST NUMBER: 1308 PRESSURE (torr): 2.0 E-6

RESULTS:

Total Mass Loss (TML):	0.58
Collected Volatile Condensable Material (CVCM):	0.02
Water Vapor Recovered (WVR):	0.18

OBSERVATIONS:

Visible Condensate:	YES	Transparent:	YES
Percent covered:	20-30%	Opaque:	NO
Thin:	YES	Interference fringes:	NO
Heavy:	NO	Color of fringes:	N/A

COMMENTS: CONDENSATE WAS LIGHT
BLUE IN APPEARANCE.

Specimen appearance after test: NO CHANGE

By:

Date:

TABLE 31g. TEST REPORT FOR MASS LOSS AND COLLECTED VOLATILE CONDENSABLE MATERIALS (NuSil Silicone Technology)



NuSil Technology
1150 Mark Avenue
Carpinteria, CA 93013
FAX 805/566-0270
805/566-0275

SAMPLE NUMBER : 3791 TEST POSITION NUMBER : 5 P.O.#: 12-20573B

CUSTOMER : IIT RESEARCH INSTITUTE
10 WEST 35TH STREET
CHICAGO, IL 60616
ATTENTION: TOM CURTIS

ASTM E-595
NASA SP-R-0022A
ESA PSS-01-702

MATERIAL TESTED: S13G/LO1 LOT: T-114
TEST DATE: 6/28/94 TEST NUMBER: 1360 PRESSURE (torr): 3.0 E-6

RESULTS: Total Mass Loss (TML): 0.37
Collected Volatile Condensable Material (CVCM): 0.02
Water Vapor Recovered (WVR): 0.11

OBSERVATIONS:
 Visible Condensate: NO Transparent: NO
 Percent covered: NO Opaque: NO
 Thin: NO Interference fringes: NO
 Heavy: NO Color of fringes: NO

COMMENTS: N/A
N/A

Specimen appearance after test: NO CHANGE

NO CHANGE

By: Jessica Jacobs

Date: 6/89/97

3.4.1 Marshall Space Flight Center (Jason Vaughn, EH11)

Combined AO and VUV tests have been conducted on all of the new, reformulated and "old" formulations at facilities at NASA/Marshall Space Flight Center (MSFC) and at Princeton University. Tests at Princeton were conducted by Mr. Vaughn (MSFC) who was also responsible for developing the facility. The features of the two systems are as follows.

Atomic Oxygen Drift Tube System (AODTS), MSFC

- Atomic oxygen plasma generated by 14.7 MHz R-F field
- Samples exposed out of R-F field eliminating any heat source
- AO neutral atoms have <0.1 eV thermal energy
- 5×10^{16} atoms/cm²/sec AO neutral flux
- NUV/VUV radiation through window ports for synergistic studies

Princeton Plasma Physics Laboratory (PPPL) System

- Plasma generated by 2.45 GHz, 1 kW R-F field confined by 4 kG magnetic field to increase flux
- VUV radiation generated by plasma thus enhancing synergism studies
- AO ions neutralized by collision with metal plate
- 3 eV to 30 eV tunable energy range
- Operated on duty cycle to maintain cool plasma source
- 10^{16} atoms/cm²/sec AO flux with 5% duty cycle
- Capable of neutral beams other than oxygen

The results for tests are summarized in Table 32, and spectral curves for the various S13G and YB-71 samples before and after exposure are shown in Figures 35 through 42. Essentially no degradation in reflectance was observed for any of the S13G/LO-1 (Figures 35 and 36) or S13GP/LO-1 (Figures 37 and 38) at either Princeton or MSFC. For the YB-71 coatings, no change was observed in MSFC tests for either the PS7 (Figure 40) or Kasil 2130

TABLE 32. RESULTS OF AO-VUV EXPOSURE OF THERMAL CONTROL COATINGS

Sample	Batch No.	Thickness, mls	Initial α	Initial ϵ	After PPPL Test ϵ	After PPPL Test α	After AODTS Test ϵ	After AODTS Test α	$\Delta\alpha$
S13G/L0-1 (PST)	S-174								
X-29		7.9	0.203	0.917					
X-30		7.3	0.209	0.917					
X-31		8.0	0.210	0.918	0.215	0.913	0.214	0.908	0.005 0.005
S13G/P/L0-1 (Kasil 2130)	S-174								
Y-20		7.8	0.204	0.908					
Y-30		7.4	0.203	0.909	0.209	0.902	0.204	0.881	0 0.006
Y-31		7.9	0.202	0.903					
YB-71 (PST)	R-123								
C-002		12.8	0.133	0.890	0.152	0.892			0.019
C-011		12.5	0.132	0.897					
C-013		12.7	0.133	0.897					-0.007
YB-71P (Kasil 2130)	S-081								
^a 10		9.1	0.124	0.888					
^a 6		9.2	0.127	0.887	0.193	0.890	0.125	0.886	0.066
^a 5		10.6	0.125	0.889					0
Z-93 (PST)	S-044								
X-33		7.4	0.145	0.909	0.149	0.918			0.004
Z-93P (Kasil 2130)	S-044								
X28		5.1	0.143	0.910	0.156	0.919			0.012

PPPL - Princeton Plasma Physics Laboratory
 $\approx 7.8 \times 10^6$ atoms/cm² AO fluence, 8000 ESH VUV

AODTS - Atomic Oxygen Drift Tube System (MSFC)
 $\approx 1 \times 10^3$ atoms/cm² AO fluence, 20,000 ESH VUV

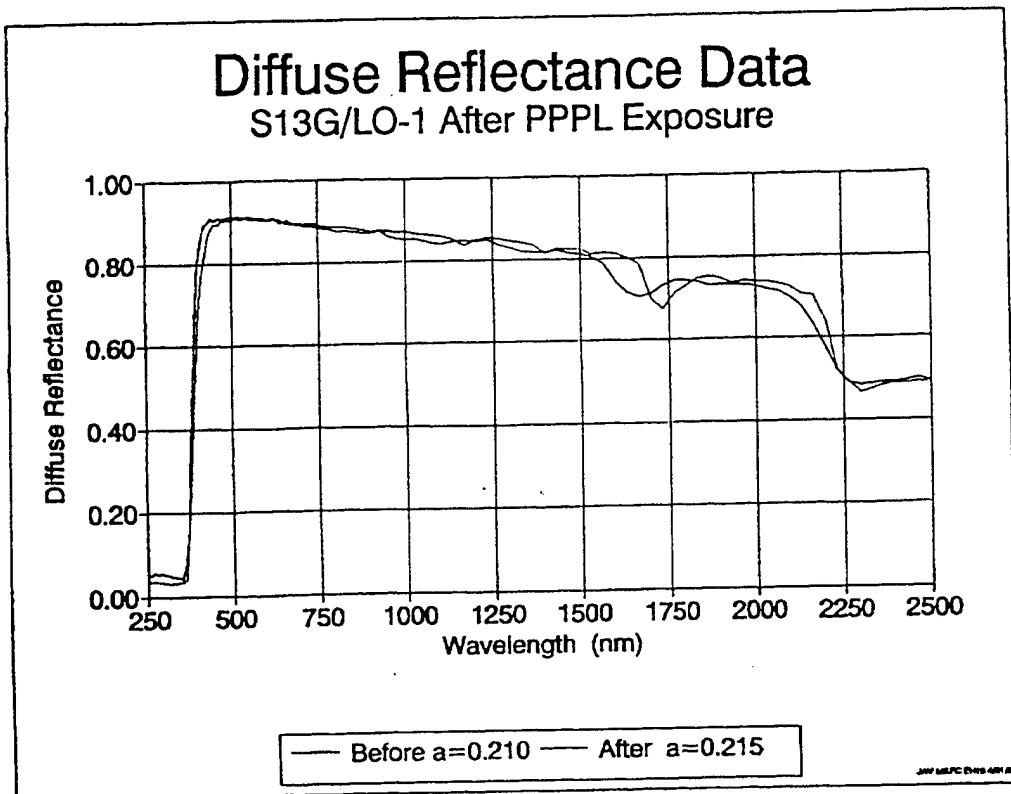


Figure 35 Diffuse Reflectance Data. S13G/LO-1 After PPPL Exposure.

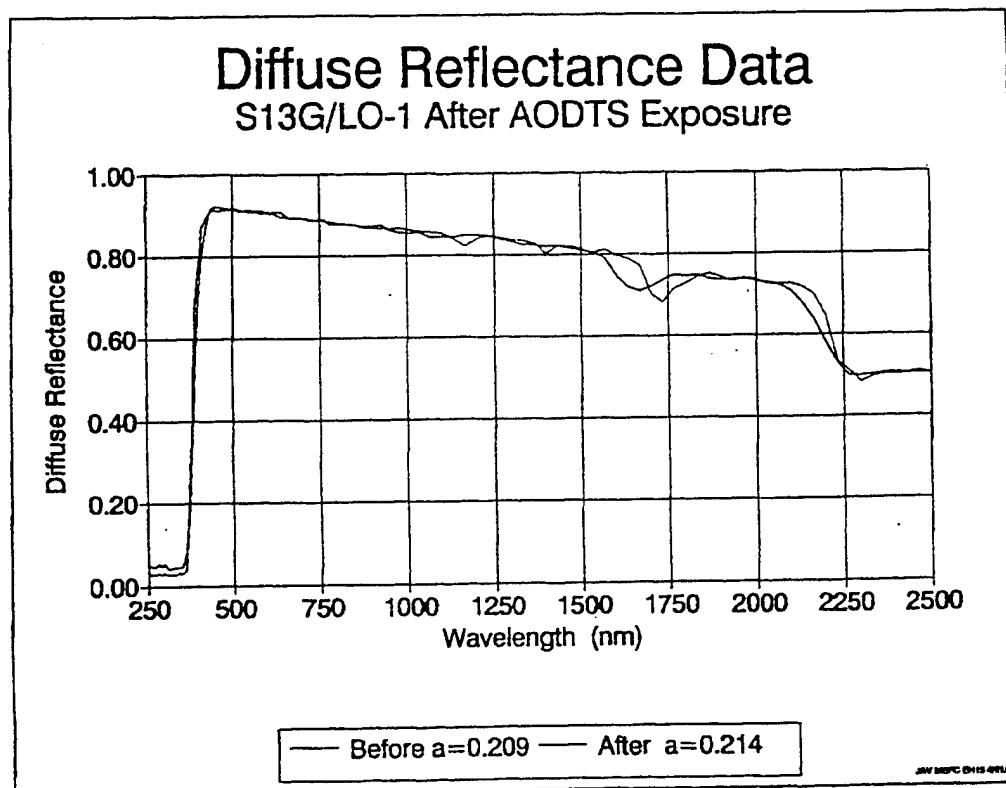


Figure 36 Diffuse Reflectance Data. S13G/LO-1 After AODTS Exposure.

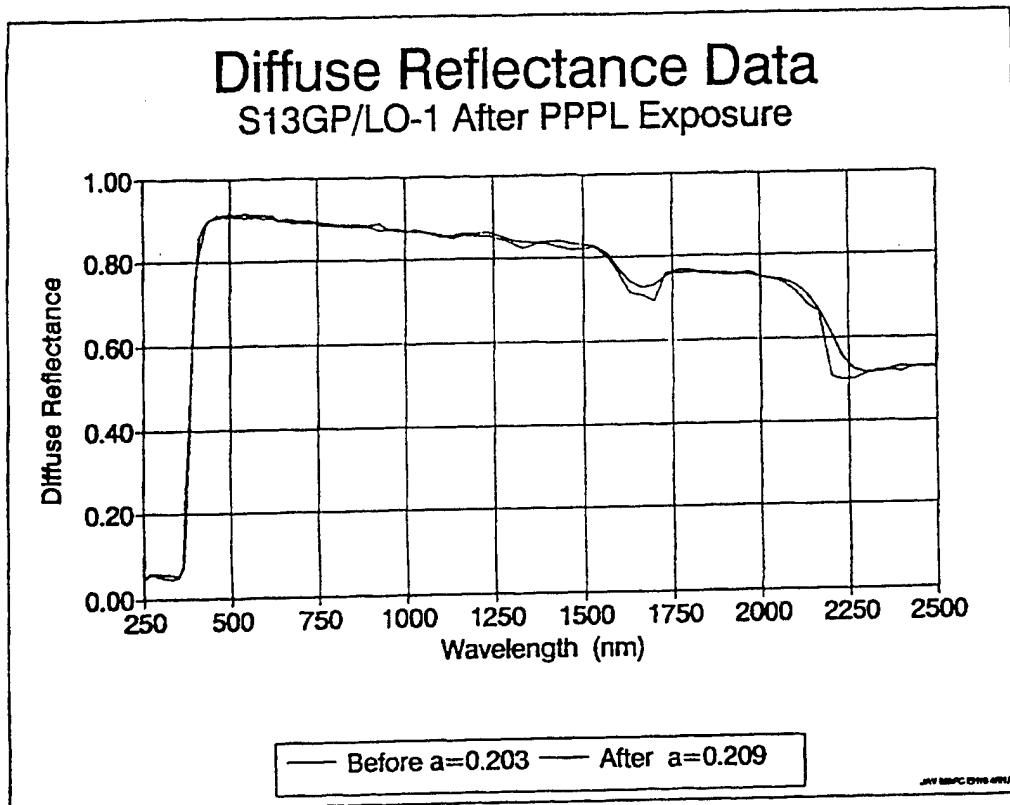


Figure 37. Diffuse Reflectance Data. S13GP/LO-1 After PPPL Exposure.

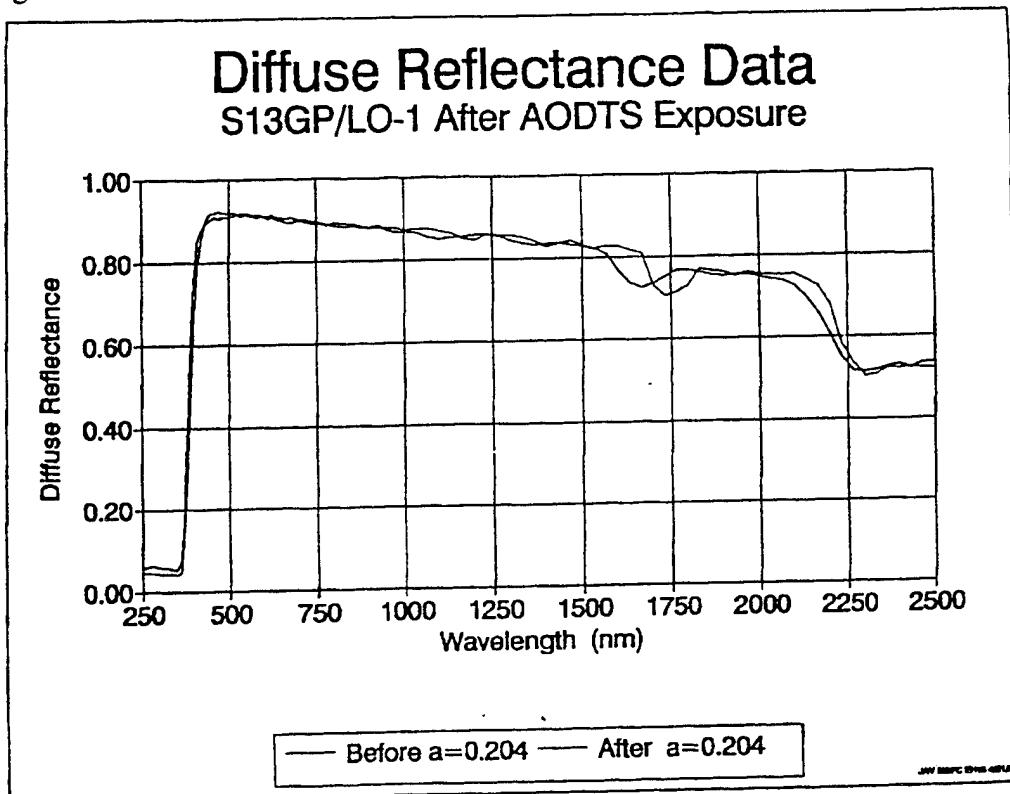


Figure 38. Diffuse Reflectance Data. S13GP/LO-1 After AODTS Exposure.

Diffuse Reflectance Data YB-71 After PPPL Exposure

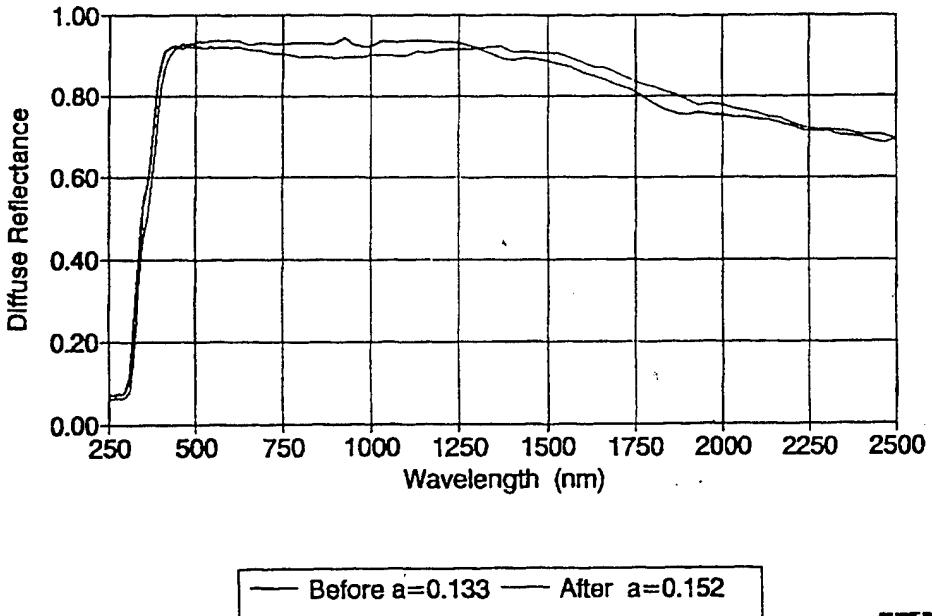


Figure 39. Diffuse Reflectance Data. YB-71 After PPPL Exposure.

Diffuse Reflectance Data YB-71 After AODTS Exposure

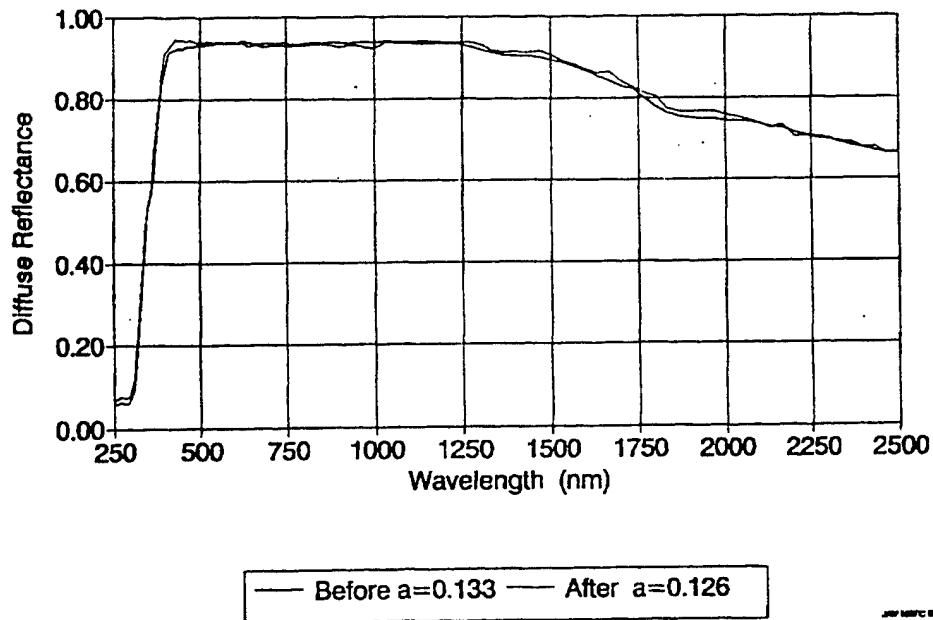


Figure 40. Diffuse Reflectance Data. YB-71 After AODTS Exposure.

Diffuse Reflectance Data YB-71P After PPPL Exposure

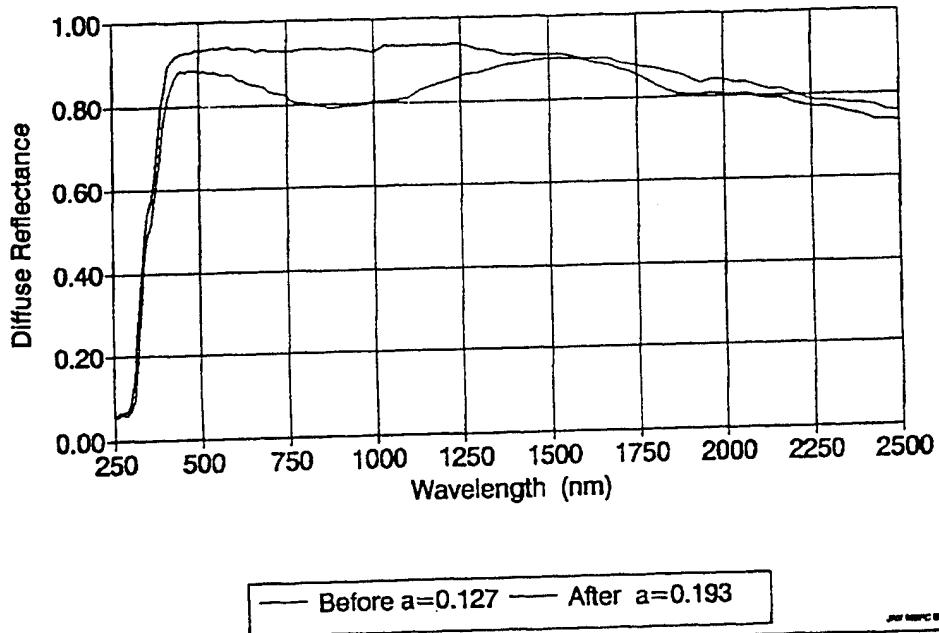


Figure 41. Diffuse Reflectance Data. YB-71P After PPPL Exposure.

Diffuse Reflectance Data YB-71P After AODTS Exposure

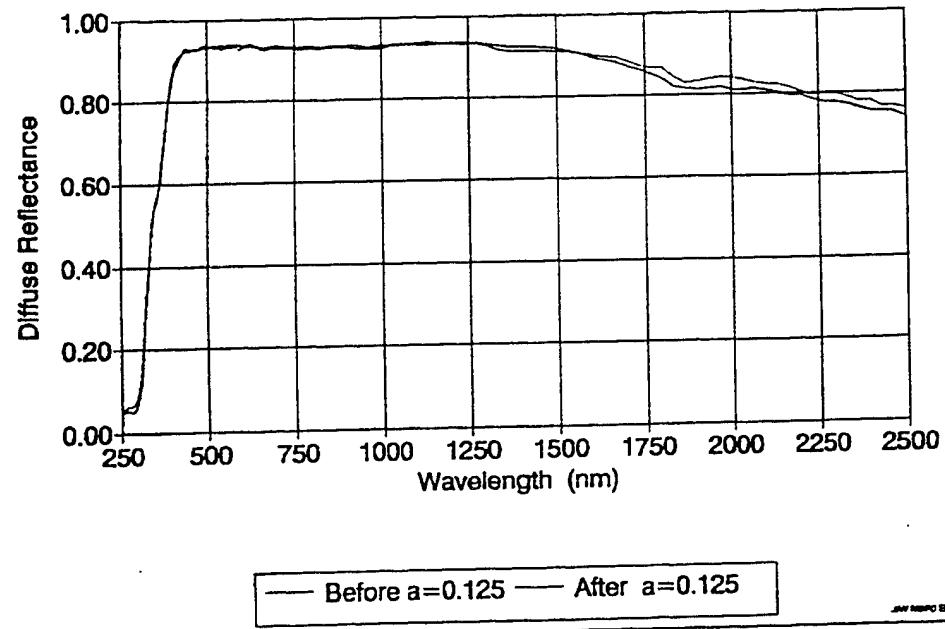


Figure 42. Diffuse Reflectance Data. YB-71P After AODTS Exposure.

(Figure 42) coatings. At Princeton, however, significant increase in α_s was seen for YB-71P (Kasil 2130) (Figure 41) and a limited increase for YB-71 (PS7) (Figure 39). Tests of Z93 at Princeton revealed very limited loss in reflectance for either the PS7 or Kasil 2130 formulations.

Conclusions which may be drawn from these AO-VUV tests are as follows:

1. Kasil 2130 encapsulated ZnO appears to be a suitable replacement for PS7 encapsulated ZnO. In addition, excellent stability in AO-VUV environment is shown by these methyl silicone compositions.
2. The use of Kasil 2130 to replace PS7 produces a Z93P composition which is as stable as Z93. This finding is reinforced by work reported by Loral Vought Systems¹⁹ and by McDonnell Douglas²⁰.
3. The use of Kasil 2130 produces a YB-71P coating which exhibits greater increase in solar absorptance than the "old" PS7/YB-71 composition. This damage is most apparent in the 900 nm region. A similar greater sensitization of zinc orthotitanate to damage by the use of Kasil 2130 binder as compared to PS7 has been observed in combined radiation tests at Wright Laboratory (Carlin, Cerbus), and at Aerospace Corporation (Meshishnek).
4. Greater optical damage was observed in the Princeton laboratory test as compared to MSFC, despite the apparent shorter exposure reported: PPPL = 8000 ESH VUV, AODTS (MSFC) = 20,000 ESH VUV.

3.4.2 Wright Laboratory (Pat Carlin)

A test designated 93QV01 was conducted at WPAFB. The electron flux rate was 3×10^9 e⁻/cm²/sec for the 10 KeV electrons and 6×10^9 e⁻/cm²/sec for the 1 KeV electrons for a total fluence of 2.5×10^{16} e⁻/cm² for over 2500 equivalent ultraviolet sun hours (EUVSH). Strong degradation was observed for YB-71P with an increase in solar absorptance (α_s) from about 0.1 to 0.4. The change observed for YB-71 in this same test was from 0.1 to 0.26. A Z93 sample exhibited a limited $\Delta\alpha_s$ of about 0.05 from 0.14 to 0.19.

A second test was conducted at WPAFB with new samples of YB-71 (Batch R-123) and YB-71P (Batch S-038), along with a duplicate YB-71P (Batch R-028) sample from the first test to check the strong degradation seen in the first test. The results show that the new set of YB-71 and YB-71P samples exhibit degradation behavior similar to that for YB-71 (Batch R-026) from the first test. The YB-71P sample from Batch R-028 displayed much stronger degradation, paralleling the behavior shown in Test 1.

The results indicate the following:

- (1) The degradation behavior observed for YB-71 type samples at WPAFB appears comparable to the data which were obtained from calorimetric experiments on the DSP system in geosynchronous orbit.⁶
- (2) Z93 appears to be more stable than YB-71 in this test environment.

Results of evaluation of YB-71 are in "18th Space Simulation Conference", "Space Mission Success Through Testing" Oct. 31-Nov. 3, 1994, NASA-CP-3280, pp 1-24, Cerbus, C.A. and Carew, P.S. Evaluation of S13G/LO-1, S13GP/LO-1, Z93, and Z93P is to be conducted in subsequent tests. Documentation of the Wright Laboratory tests are to be produced by Carlin et al.

3.4.3 Aerospace Corporation (Mike Meshishnek)

Combined radiation tests are being conducted at the Aerospace Corporation. The results from an initial UV-vacuum test of 2300 ESH with electron fluences of 8.5×10^{15} at 10 KeV and 1.7×10^{16} at 1 Kev are shown in Table 33. These data show the following:

**TABLE 33. RESULTS OF VACUUM-UV, ELECTRON IRRADIATION
OF THERMAL CONTROL COATINGS (Aerospace Corporation)**
(2300 ESH, $2.5 \times 10^{16} e^-$)

Coating	Batch	Aerospace Sample Nr.	Solar Absorptance, α_s		
			Initial	Final	Δ
Z93	R009	5	.12	.15	.03
		12	.12	.15	.03
Z93P	R016	6	.13	.16	.03
	S043	7	.11	.13	.02
	S043	13	.11	.15	.04
S13G/LO-1	Q090	8	.18	.24	.06
S13GP/LO-1	R055	9	.15	.23	.08
	R055	16	.15	.20	.05
YB-71	R026	1	.12	.20	.08
	R123	3	.09	.14	.05
	R123	10	.09	.13	.04
YB-71P	R028	2	.11	.23	.12
	R028	11	.11	.23	.12
	S038	4	.09	.18	.09

- (1) Z93 and Z93P samples exhibit similar initial solar absorptance values and similar losses in reflectance, indicating that Kasil 2130 is a good substitute for PS7. The Z93 materials also appear to be more stable than the S13 type or YB-71 coatings.
- (2) S13G/LO-1 and S13GP/LO-1 samples also exhibit similar α_s and $\Delta\alpha_s$ values, indicating that Kasil 2130 is a good substitute for PS7 as an encapsulant for ZnO pigment. The reflectance losses were somewhat greater than that for Z93 coatings, and of similar magnitude to that for YB-71.
- (3) The YB-71 and YB-71P coatings exhibit a lower initial solar absorptance as compared to the S13 and Z93 materials. The YB-71P materials were less stable than YB-71 as was observed at the Princeton facility and at Wright Laboratory. As previously stated, Kasil 2130 does not appear to be an adequate substitute for PS7 on a simple replacement basis. Compositional refinements are needed to obtain an acceptable second generation YB-71.

A second and third electron-UV-vacuum tests have been conducted at the Aerospace Corporation. Dr. Meshishnek will prepare detailed documentation and analyses of his studies.

3.4.4 Loral Vought Systems (Joe Stoyack)

Z93 formulations involving different potassium silicate binders, PS7 (Sylvania) and Kasil 2130, Kasil 2135, and Kasil 1 (PQ Corporation) were evaluated at LVS. These studies determined physical properties such as viscosity, sprayability, optical properties, thickness control, adhesion, and thermal shock resistance for all of the above-listed Z93 formulations.

Simulated space environment tests were conducted for LVS by NASA-Lewis in their Directed Atomic Oxygen/VUV Exposure Facility. The various Z93 formulations for these tests were prepared both at LVS and at IITRI. The best binder material emerging from these space environment tests was Kasil 2130, which is the binder material for IITRI's Z93P. LVS also determined the Z93P composition to be the best requalified Z93, based on the evaluations of physical and optical properties as well as the space simulation tests. Details of the LVS studies are contained in a document, "Z93 Reformulation Evaluation," J. E. Stoyack, DIR. No. 3-47300H/3DIR-016, dated 1/31/94.¹⁹

3.5 SPACE-FLIGHT TESTING

Samples of all requalification candidate coatings were submitted to Dr. David Zimcik of the Canadian Space Agency for inclusion in the STS-52 experiment entitled "Materials Exposure in Low Earth Orbit (MELEO)." We have been unable to obtain any report on the results except a verbal communication that "all exposed samples showed no optical or physical degradation." The limited optical data provided are somewhat suspect in that the absolute solar absorptance values for all samples were very low, e.g., Z93 and Z93P with values of 0.05 to 0.07. Our last request for information from Dr. Zimcik revealed that the Canadian Space Agency was undergoing reorganization and geographical changes so that the MELEO results might not be finalized. In addition, the experiment was thought to have been contaminated during flight.

A more promising avenue to space-flight exposure appears to be the Space Active Modular Materials Experiment (SAMMES). Requalification (Kasil 2130) coating samples have been prepared on calorimetric discs and cups and submitted to the Aerospace Corporation (Dr. Mike Meshishnek) for inclusion in this flight experiment. Launch of this experiment is anticipated for 1995.

4. SUMMARY AND CONCLUSIONS

The purpose of this program was to develop requalified spacecraft thermal control coating formulations utilizing an alternate potassium silicate binder solution to replace Sylvania's PS7 product which is no longer manufactured. Our studies to reformulate IITRI's solar reflectors—Z93, S13G/LO-1 and YB-71—have resulted in the following developments:

1. The substitution of PQ Corporation's Kasil 2130 for Sylvania's PS7 in the Z93 formulation produces coatings (Z93P) which are equivalent or superior to the original Z93 in physical, mechanical, and optical properties, and in stability to a space environment.
2. The substitution of Kasil 2130 for PS7 in the encapsulation process for coating zinc oxide pigment particles, yields a S13GP/LO-1 composition which is equivalent in processing behavior and in properties to the original S13G/LO-1. In addition, a superior stability to the space environment is indicated for the reformulated silicone composition as compared to the older S13G/LO.
3. The use of Kasil 2130 as a binder replacement for PS7 in the YB-71 composition results in coatings (YB-71P) which exhibit processing behavior, physical, mechanical and optical properties similar to those for YB-71. However, YB-71P exhibits decreased resistance to optical degradation in a space environment, particularly under electron irradiation.
4. The reformulated Z93P and S13GP/LO-1 incorporating Kasil 2130 appear to be satisfactory replacements for Z93 and S13G/LO-1 which utilized PS7. Additional studies are required to develop a YB-71P composition which will be as stable to the space environment as YB-71.

5. RECOMMENDATIONS FOR FUTURE WORK

- (A) The work performed on this program has produced satisfactory replacements for Z93 and S13G/LO-1. There is a need for additional studies to accomplish similar results with the YB-71 (ZOT) formulation. Exploratory studies in our laboratories have indicated directions for passivating the surfaces of ZOT particles to achieve resistance to particulate and UV irradiation of space. These proposed studies will also explore silicate chemistry and its effect on the optical behavior of thermal control coatings. It is recommended that a program be conducted to develop a YB-71P which would be a reliable solar reflector offering the following advantages:
1. Lower initial solar absorptance of about 0.10;
 2. Harder, more cleanable coating surfaces;
 3. Electrical conductivity behavior which would prevent charge buildup but would not interfere with desired communication characteristics.
- (B) The impetus for this program was the unavailability of a key component, potassium silicate, for spacecraft solar reflector coatings. Substitute formulations have been developed in the form of Z93P and S13GP/LO-1, but these are single formulations. It is strongly recommended that research and development be performed so that other satisfactory materials are available, circumventing or at least alleviating the vagaries of the market place. This R&D would involve the following:
1. Use of different alkali silicates, e.g., sodium silicate, and different commercial second sources where available;
 2. Determination of alternate sources of ZnO pigment and characterization of these powders;
 3. Laboratory synthesis capability for producing alkali silicates and/or methyl silicones;

4. Development of alternate thermal control coatings so that disappearance of any single composition would have minimal impact on projected satellite use.
- (C) Another area that deserves strong consideration is the complete characterization of properties for different thermal control coatings. This would include thermal and electrical properties which are solely needed by designers for adequate modelling and planning. Reaction of different materials to varying combined environmental irradiation conditions needs to be established, in particular for the more extended mission lifetimes and more rigorous environments to be encountered.

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